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SUPPLEMENT TO THE CHEMICAL NEWS, JULY 3, 1891.

THE
CHEMICAL NEWS

AND
JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO
PHARMACY, ARTS, AND MANUFACTURES.

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THE CHEMICAL NEWS.

VOLUME LXIII.

EDITED BY WILLIAM CROOKES, F.R.S., &c.

No. 1623.—JANUARY 2, 1891.

ON A
**DETERMINATION OF THE BOILING-POINT
OF SULPHUR,**
AND ON A
**METHOD OF STANDARDISING PLATINUM
RESISTANCE THERMOMETERS BY
REFERENCE TO IT.***

By HUGH L. CALLENDAR, M.A., Fellow of Trinity College,
Cambridge, and E. H. GRIFFITHS, M.A., of Sidney Sussex
College, Cambridge.

EXPERIMENTS by different observers have shown that electrical resistance thermometers afford the most convenient and accurate method of measuring temperature through a very wide range. By selecting a particular thermometer as the standard, and directly comparing others with it, it has been found possible to attain a degree of accuracy of the order of 0.001° in the relative measurements between 0° and 100°C. , and of the order of 0.01° at 450°C.

In a previous communication† it has been shown that, if t be the temperature by air thermometer, and if pt be the temperature by platinum resistance thermometer, the difference between them is very closely represented from 0° to 700°C. by the formula—

$$d = t - pt = \delta \left\{ \frac{t}{100} \right\}^2 - \frac{t}{100} \dots (d).$$

The value of the constant δ for a particular wire was found to be 1.570.

The object of the present paper is to describe a method of finding the value of this constant for any such thermometer, by means of a single observation at some known fixed point other than 0° or 100°C.

The boiling-point of sulphur happens to be the most convenient for this purpose. We have therefore made a careful determination of this point by reference to the standard air thermometer, and have given a full description of the method and apparatus which we have found most suitable for standardising platinum thermometers by means of it.

The paper is divided into three parts.

Part I. contains a description of the method and apparatus employed in comparing the platinum thermometers used in this investigation with the air thermometer at a temperature very near the boiling-point of sulphur.

Part II. contains the determination of the actual boiling-point of sulphur by means of the thermometers thus standardised, and a description of the method and

apparatus to be used in standardising [other] platinum thermometers. A table is also given reduced from a previous series of observations of other fixed points which may be used for the same purpose.

Part III. contains a comparison of the platinum and air thermometers between 0° and 100° , and shows that the δ -formula holds accurately between those limits.

The determination of the boiling-point of sulphur was made by means of three platinum thermometers, L , M_1 , and M_2 , constructed out of the wire used in the experiments of 1887, before referred to.

Full descriptions of these thermometers are given in the paper. They were furnished with double electrodes for measuring the resistance of the connecting wires at each observation, their insulation was carefully tested, and all due precautions were taken to guard against thermal effects and other sources of error.

Thermometers M_1 and M_2 were standardised by direct comparison with an air thermometer at the boiling-point of sulphur. Full particulars are given of the details of the observations and calculations, showing the limits of error of the experiments.

The expansion of the glass forming the bulb of the air thermometer was determined both by the method of linear expansion, and also by using the bulb itself as a mercury weight thermometer. The values found by the two methods agreed very closely.

The small changes of the volume of the bulb were determined from time to time during the progress of the experiments. The final observations were not taken till the thermometer had reached a fairly steady state.

The limit of accuracy attainable with this air thermometer was found to depend chiefly on that of the barometric readings. The barometer used was therefore verified by a careful comparison with the standard metre scale.

The iron-tube apparatus in which the platinum and air thermometers were compared was so constructed as to be capable of being maintained at a constant temperature by a steady flow of sulphur vapour for any length of time.

Observations were taken with it on two separate days. On each occasion the temperature was kept steady to 0.1° for about two hours. Allowing for the difference of the atmospheric pressure, the temperature attained was the same on both days.

The results of the comparison were in perfect agreement with the experiments of 1887, and showed that the δ -coefficient of the wire had not altered appreciably in the interval.

The apparatus which we have found most convenient for standardising platinum thermometers by means of the boiling-point of sulphur consists of a wide glass tube, 40

* Abstract of a Paper read before the Royal Society, Dec. 18, 1890.
† Callendar, *Phil. Trans.*, A., 1887, p. 161.

c.m. long and 4 c.m. in diameter, with a spherical bulb at the end. Tubes of this kind are commonly used to heat Victor Meyer's vapour-density apparatus. For brevity we have called it a "Meyer" tube.

The outside of the tube is thickly padded with asbestos wool, with the exception of the lower half of the bulb, and of a short length of 3—5 c.m. at the top, which serves as a condenser. The tube is filled with sulphur to a level of 3 or 4 c.m. above the bulb, and is heated by a Bunsen burner. The gas is adjusted so as to keep the level of the vapour near the top of the tube, which is covered with asbestos card to prevent the sulphur catching fire.

Our experiments have shown that a thermometer inserted in an apparatus of this kind will not attain the actual temperature of the vapour, unless it is protected from radiation to the sides of the tube, and from the condensed liquid which runs down the stem. The lowering of temperature due to radiation, &c., may readily amount to upwards of 2° at the boiling-point of sulphur.

The method which we have adopted for screening the thermometer is to bind an umbrella of asbestos card on to its stem a short distance above the bulb. Two coaxial tubes are hung on to this umbrella to screen the thermometer from radiation. We have found that glass is not sufficiently opaque to heat radiation at this temperature. The inner tube at least should be of metal.

To avoid superheating of the vapour, it is necessary to make sure that the level of the liquid sulphur stands well above that part of the bulb which is exposed to the flame.

Using these precautions, we have found that the temperature by normal air thermometer at constant pressure of the saturated vapour of sulphur, boiling freely under a pressure of 760 m.m. of mercury at 0° C. and $g = 980.61$ C.G.S. (sea level in lat. 45°), is—

$$t = 444.53^{\circ} \text{C.}$$

The value given by Regnault* is nearly 4° higher than this; but in the account which he gives of his experiments he has pointed out several sources of error, and it is evident that he did not place much confidence in his results.

The close agreement between the air thermometer experiments of 1887 and the present series leads us to conclude that the number above given is probably correct to a tenth of a degree, and that it may be safely used for standardising platinum thermometers.

The method which we recommend for standardising platinum thermometers is briefly as follows:—Observe the value R_s of the resistance in sulphur vapour in an apparatus such as we have described. Calculate the value of θt_s by the formula—

$$\theta t_s = 100 (R_s - R_0) / (R_{100} - R_0).$$

Find the temperature t of the sulphur vapour, corresponding to the corrected barometric pressure H_0 , from the formula—

$$t = 444.53 + 0.082 (H_0 - 760).$$

The appropriate value of δ is then given by the equation—

$$t - \theta t_s = \delta \left\{ \frac{t}{100} - \frac{t_s}{100} \right\}.$$

We have made use of this method to reduce the results given in a previous communication,† "On the Determination of some Boiling and Freezing Points by means of the Platinum Thermometer," and we find that the values of t deduced from the observations with several thermometers of different patterns and with very different coefficients, are in remarkably close agreement. The results found with the three best thermometers are given in the following table:—

Table of Boiling and Freezing Points Reduced by Formula (d).

Nature of experiment.	Thermometers used.			Mean.
	E.	F.	G.	
Boiling-point of—				
Aniline (760 m.m.)	184.11	184.13	184.14	184.13
Naphthalene.. .. "	217.88	217.96	217.98	217.94
Methyl salicylate .. "	222.98	223.08	—	223.03
Benzophenone .. "	305.82	305.87	305.78	305.82
Triphenyl methane				
(770.8 m.m.)	356.47	—	356.41	356.44
Mercury.. .. (760 m.m.)	356.74	356.82	356.71	356.76
Freezing-point of—				
Tin	231.66	231.66	231.73	231.68
Bismuth	269.18	—	269.25	269.22
Cadmium	320.70	—	320.66	320.68
Lead	327.66	—	327.71	327.69
Zinc	417.55	—	417.59	417.57

The fixed points given in the above have not been so carefully determined as the boiling-point of sulphur. They rest entirely on the assumption of the accuracy of the δ -formula, and have not been directly referred to the air thermometer. We believe, however, that they are probably correct to 0.1° C., and that they may be safely used to standardise thermometers of limited range, in cases where it may happen to be inconvenient to make use of the sulphur point.

In comparing the platinum and air thermometers between 0° and 100° C., observations were taken at intervals of 5° all the way up. The mean deviation of the observations from the parabolic formula (d) is only 0.006°. This corresponds to the limit of accuracy of the barometric readings, and there is no reason to suppose that the δ -formula may not represent the difference even more closely than this.

The same platinum thermometer has been compared with several mercury thermometers standardised at Kew.* The result seems to show that the Kew standard reads 0.1° C. lower than our air-thermometer at 30°.

THE VARIATIONS OF ELECTROMOTIVE FORCE OF CELLS CONSISTING OF CERTAIN METALS, PLATINUM, AND NITRIC ACID.†

By G. J. BURCH, B.A., and V. H. VELEY, M.A., the University Museum, Oxford.

THE description of the apparatus, the capillary electrometer, and the method of working are given fully in the paper. The following conclusions are drawn from the results of the experiments:—

I. When the metals copper, silver, bismuth, and mercury are introduced into purified nitric acid of different degrees of concentration, and a couple made with platinum, the electromotive force of such a cell increases considerably until it reaches a constant and (in most cases) a maximum value. The rise of E.M.F. is attributed to the production of nitrous acid by the decomposition of the nitric acid, and the final value is considered to be due to the former acid only, while the initial value is due for the most part to the latter acid, though it is affected to a remarkable degree by the amount of impurity of nitrous acid, either initially present or produced by minute and unavoidable uncleanness of the metallic strip and the containing vessel.

II. If nitrous acid has been previously added to the nitric acid, then the maximum E.M.F. is reached at once.

III. If the conditions, namely, increase of temperature, of impurity, and of concentration of acid, are such as

* Mémoires de l'Institut, vol. 26, p. 526.

† Griffiths, Phil. Trans., A, 1890.

* Griffiths, "Brit. Assoc. Report," 1890.

† Abstract of a Paper read before the Royal Society.

would favour a more rapid solution of the metal, and consequently a more rapid production of nitrous acid, then the rise of E.M.F. is concomitantly more rapid.

IV. Conversely, if the conditions are unfavourable to the production of nitrous acid, the rise of E.M.F. is less rapid.

V. If any substance, such as urea, be added which would tend to destroy the nitrous acid as fast as it may be formed, then the rise of E.M.F. is extremely slow, being dependent upon the number of molecular impacts of the nitrous acid upon the surface of the metal.

Thus the results obtained by the electrometer and by the chemical balance are in every way confirmatory the one of the other.

The authors propose to conduct further investigations on cells containing other acids, to determine whether the action of them upon metals is conditioned by the presence of their products of electrolysis.

THE CONDITIONS OF CHEMICAL CHANGE BETWEEN NITRIC ACID AND CERTAIN METALS.*

By V. H. VELEY, M.A., the University Museum, Oxford.

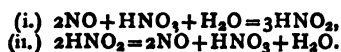
THIS paper is in continuation of a preliminary communication on the same subject; the main points contained in it are as follows:—

I. The metals copper, mercury, and bismuth do not dissolve in nitric acid of about 30 per cent concentration (the acid commonly employed for the preparation of nitric oxide gas) and heated to a temperature of 30° C., provided that nitrous acid is neither present initially nor formed subsequently. To prevent this it is necessary in the cases of copper and bismuth to add a small quantity of some oxidising substance, such as hydrogen peroxide or potassium chlorate, or, as less efficacious, potassium permanganate, or to pass a current of air or, lastly, such a substance as urea, which destroys the nitrous acid by its interaction.

II. If the conditions are such that these metals dissolve, then the amount of metal dissolved and the amount of nitrous acid present are concomitant variables, provided that the nitric acid is in considerable excess. Change of conditions, such as concentration of acid and variation of temperature, which increase the former increase also the latter.

III. If the conditions are such that these metals dissolve, it would appear that the metallic nitrite is at first formed, together with nitric oxide; the former is decomposed by the excess of nitric acid to liberate nitrous acid, while the latter reduces the nitric acid to form a further quantity of nitrous acid.

Eventually the net result is the product of two reverse chemical changes represented by the equations—



The nitrous acid is thus destroyed as fast as it is generated.

IV. If the conditions are such that metals dissolve in nitric acid, then nitrous acid is invariably the initial product of reduction.

V. The metals copper, mercury, and bismuth dissolve very readily in a 1 per cent solution of nitrous acid; under these conditions nitric acid present in slight excess interferes with, rather than promotes, the chemical change. This result is probably due to the greater stability of nitrous acid in the presence of nitric acid.

VI. Hydrogen gas reduces nitric to nitrous acid in presence of cupric or lead nitrate; it also converts

mercuric into mercurous nitrate, but does not produce any change in solutions of bismuth and zinc nitrates dissolved in nitric acid.

FRICITION OF GASES IN PIPES.

By Dr. L. C. LEVOIR, Polytechnicum, Delft.

THE introduction of gaseous fuel in factories compels lecturers in technical colleges to discuss a series of quite new laws. In all the old treatises on Physics and Chemistry no experiment is related that might give a large audience an idea of the diminution in pressure on conducting gases through tubes. In the *CHEMICAL NEWS* for August 3rd, 1861 (vol. iv., p. 60), and *Dingler's Polytechnisches Journal* (German), 1861, I described an experiment to show that friction of smoke in a chimney is higher in a conical one when the widest end is used as inlet.

Two small gas-flames on the same T-shaped gas-pipe, with very low pressure of the gas, gave me an opportunity to show that one of the flames was nearly invisible on the opposite side from where the chimney (1 metre in length, and 2 and 5 centimetres in diameter) drew with the highest force.

But there is a still more sensitive test for difference in exhausting power,—that is, in every Bunsen's burner of great size the inlet for the air must be regulated in the stand, that the flame cannot burn on the top, but detonates always downwards from too great admixture of air. A small end of tube placed in the air-holes directly stops that explosion, by causing friction therein and diminishing the quantity of air admitted.

Evidently this is a way to show to a large audience the friction of smoke in chimneys and gas in tubes, which is so difficult a point both in the education of physicists and engineers.

ON GASEOUS ILLUMINANTS.*

By Professor VIVIAN B. LEWES.

I.

JUST 200 years after Van Helmont (in the seventeenth century) first used the term "gas" to describe æriform bodies, Faraday defined a gas as being the vapour of a volatile liquid, existing at a temperature considerably above the boiling-point of the liquid, and that the condensing-point of the gas was merely the boiling-point of the liquid producing it. This definition was contested at the time, as several of the gases had not then been condensed; but now it is known that the condensation of any gas to the liquid form is merely a question of sufficiently intense cold, and pressure.

Hydrogen and the gaseous compounds of carbon and hydrogen have so strong an affinity for the oxygen contained in the atmosphere, that the heat emitted by a burning match is generally sufficient to determine combination between the gases; and where the heat evolved by the combination is sufficient to raise the gases or vapour to incandescence, the phenomenon of flame is the result. Some flames have the power, under certain conditions, of emitting light, while others have no photometric value; and it is a matter of the gravest importance to the gas world that as clear a conception as possible should be obtained of the conditions and cause of luminosity in flames. A visible flame may either be solid—that is to say, composed of a solid mass of incandescent particles—or it may have a distinctive internal structure, and show zones in which varying phases of combustion are taking place; and it is to this latter class

* Abstract of a Paper read before the Royal Society.

* Abstract of the Cantor Lectures delivered at the Society of Arts Communicated by the Author.

that all flames produced by a gas issuing from a burner belong.

In the *Philosophical Magazine* for 1817 Sir Humphry Davy says, while alluding to a paper published in one of the early numbers of the *Journal of Science and Arts*: "I have given an account of some new results on flame which show that the intensity of the light of flames depends principally upon the production and ignition of solid matter in combustion."

His theory, however, has gradually been altered by frequent quotation, until it is more often given as "the presence of solid particles suspended in the flame (or in immediate contact with the burning gas) is essential to its luminosity"—an idea which Davy never had, as is shown by him later in the paper defining flame as follows:—"Flame is gaseous matter heated so highly as to be luminous;" and again: "When in flames, pure gaseous matter is burnt, the light is extremely feeble." Moreover, he alludes to "common flames"—evidently meaning the flames of candle, lamps, or gas; in all which cases I think it can be proved beyond a doubt that his theory, as expounded by himself, was perfectly correct. On June 11, 1868, Professor E. Frankland read a communication before the Royal Society, in which he described experiments which led him to doubt Sir Humphry Davy's theory. He points out that the deposit of soot formed when a cold surface is held in a gas or candle flame is not pure carbon, but contains hydrogen, which can only be got rid of by prolonged heating in an atmosphere of chlorine. Also that many flames possessing a high degree of luminosity cannot possibly contain solid particles. Arsenic burnt in oxygen gives a bright white light; yet as arsenic volatiles at 180° C., and the arsenic trioxide forms at 218° C., it is evident that at the temperature of incandescence (which is at least 500° C.) there can be no solids, but simply vapours present in the flame; and for the same reason, the intense light resulting from the burning of phosphorus in oxygen cannot be explained by the solid particle theory. From these results Dr. Frankland considers that "incandescent particles of carbon are not the source of light in gas and candle flames, but that the luminosity of these flames is due to radiations from dense but transparent hydrocarbon vapours;" and he further shows that non-luminous flames, such as that produced by carbon monoxide and hydrogen, can, when burning in an atmosphere of oxygen, be rendered luminous if the ordinary atmospheric pressure is increased to 10 atmospheres, so as to prevent or retard as far as possible expansion during combustion. From Dr. Frankland's experiments, there is no doubt that the luminosity of a flame is increased by pressing around it the atmosphere in which it is burning, and also that rarefaction has the opposite effect—a point also worked at by Davy; but his experiments do not show that incandescent particles of carbon are not the principal source of luminosity in a gas flame. He also shows that the higher the density of the vapours present in a flame, the more likely is it to be luminous.

In 1874, Soret attempted to demonstrate the existence of solid particles in a luminous hydrocarbon flame, by focussing the sun's rays on the flame, and examining the reflected light by means of a Nicol prism; but neither his research nor that of Burch, who repeated his experiments, using the spectroscope instead of the prism, showed more than that solid particles are present. Herr W. Stein, in considering Dr. Frankland's objections to Davy's theory, pointed out that the soot which is deposited from a candle or gas flame, and which Frankland looked upon as a condensed hydrocarbon, contains 99.1 per cent of carbon and only 0.9 per cent of hydrogen, which is about the quantity of hydrogen one would expect to be occluded by carbon formed under these conditions, and he also pointed out that if the soot were a heavy hydrocarbon condensed by a cold surface, cooling the vapour present in the flame, it ought to again become volatile at a high temperature, which it does not. The next steps in the

controversy were the attempts made by Hilgard, Landolt, and Blochman to trace the actions taking place in various flames by withdrawing the gases from different parts of the flame and determining their composition. Experiments which show that with ordinary gas it is the hydrogen which burns first, whilst the heavy hydrocarbons become gradually reduced by the heat of the flame into simpler compounds until in the luminous zone of the flame they are broken down into carbon and methane, and it is the carbon in excessively minute particles which at the moment of liberation is heated to incandescence, and "principally" gives the light of the flame—the marsh gas originally present, and also that formed from the heavier hydrocarbons, adding its quota to the luminosity by still further decomposition during combustion, and finally becoming carbon dioxide and water. In 1876, Dr. Karl Heumann made a most important contribution to the theory of luminous flames in some papers published in Liebig's *Annalen*, in which he carefully went over the work of previous observers, and, by a large number of original experiments, proved that Davy's theory was correct, but that other causes also affected the degree of luminosity in a gas or candle flame.

In the ordinary atmospheric burner in which a mixture of coal-gas and air burn with a non-luminous flame, it was supposed that the admixture of air, by supplying oxygen to the inner portion of the flame, caused immediate and complete oxidation of the hydrocarbons, without giving time for the liberation of carbon in the flame, and consequently luminosity. More modern researches, however, have proved this to be utterly wrong. The loss of luminosity is due to two causes—first, to the diluting action of the air introduced; secondly, to the fact that when a gas is so diluted it requires a far higher temperature to break up the hydrocarbons present than when the gas is undiluted, and therefore the temperature which serves to liberate carbon and render the undiluted gas-flame luminous, is totally insufficient to do so in the diluted gas. Consequently the hydrocarbon burns to carbon dioxide and water without any such liberation, and hence with a non-luminous flame. The truth of this theory can be easily proved by the fact that diluting the gas with nitrogen, carbon dioxide, or even steam, serves to render it non-luminous, and therefore more rapid oxidation has very little or nothing to do with it, while the non-luminous flame can again be rendered luminous either by heating the mixture of air and gas just before combustion, or by heating the air with which the gas is diluted. This being so, it is evident that in the non-luminous flame we have the same hydrocarbon present as in the luminous flame; and anything that will tend to break them up, and liberate the carbon before the hydrocarbons are consumed, should again make the flame luminous. That heat will do this has been already shown; but it can be demonstrated in a still more striking way. It is well known that chlorine gas and bromine vapour will both support the combustion of a gas containing much hydrogen, but that the combustion is very different from that of the same gas burning in air, as the chlorine or bromine, having no affinity for the carbon, combines with the hydrogen only, and deposits the carbon in clouds of soot; in other words, at the temperature of flame, chlorine will break up the hydrocarbons and liberate solid carbon. If now a small quantity of chlorine is led into the non-luminous Bunsen flame, it at once becomes luminous; proving conclusively that luminosity is due to solid particles of carbon liberated in the flame. Again, Heumann points out that a small rod held in the luminous flame becomes rapidly covered on its lower side with a deposit of soot; that is to say, the soot is present in particles in the flame, and the uprush of the gas drives it against the rod and deposits it there. If the soot were present in the flame, as Frankland supposed, in the state of vapour, and the rod merely acted by cooling and condensing it, the soot should be deposited on all sides of the

rod; while a still further proof is that if the soot existed as vapour in the flame, then if the rod were heated to a high temperature no soot should be deposited on it, whereas the soot deposits on a heated surface just as well as on a cool one.

It has been objected to the "solid particle" theory that, if it were true, solid carbon particles introduced into a non-luminous flame should render it luminous and make it look like an ordinary gas-flame, whereas it simply gives rise to a cloud of sparks. But it must be remembered that the "nascent" carbon, as it is liberated from the decomposing hydrocarbons, is in the molecular condition, and has a very different degree of coarse-grainedness to any preparation of charcoal or lampblack we can make; and that, although our finest particle is a mass which takes so long to burn that it leaves the flames only partly consumed, and is projected into the air as a spark, the molecular particles of carbon are consumed as soon as they are rendered incandescent, and a steady luminosity, free from sparks, results. It is possible, however, to make the particles in a luminous flame roll themselves together, when they can be either deposited in a very coarse kind of soot, or be seen as glowing sparks and particles in the mantle of the flame. This can be done when two luminous flames are allowed to rush against each other or against a heated surface. Heumann also shows that the luminous mantle of a flame is not altogether transparent, and that the thicker the flame-layer, and the greater the number of solid particles contained in it, the less transparent does it become. If a non-luminous flame—say hydrogen—is charged with the vapour of chromyl dichloride (CrO_2Cl_2), chromic oxide is produced; and this flame, which undoubtedly contains solid particles, is quite as transparent as the hydrocarbon flame. Finally, those flames which undoubtedly owe their luminosity to the presence of finely divided solid matter produce characteristic shadows when viewed in sunlight; the only luminous flames which do not throw shadows being those which consist of glowing vapours and gases. Luminous gas-flames, oil-lamp flames, and candle flames produce strongly-marked shadows in sunlight, and therefore contain finely-divided solid matter; and that this can be nothing but carbon is evident from the fact that all other substances capable of remaining solid at the temperature of the flames are absent.

From the foregoing considerations, it must be admitted that Sir Humphry Davy's statement that the intensity of the light of flames (such as those produced by candles, oil, or gas) depends principally upon the production and ignition of solid matter in combustion, was undoubtedly the true one; and it must also be borne in mind that the degree of luminosity of a flame is affected by the constituents of the gas other than the heavy hydrocarbons—some, like marsh-gas, although ordinarily burning with an apparently non-luminous flame, and separating no soot, adding considerably to the luminosity at the temperature of the flame, while others, like carbon monoxide, reduce it.

The luminosity of a flame is increased by an increase of density in the media in which it is burning, and is decreased by rarefaction—an effect supposed by Dr. Frankland to be owing to the alteration of density and alteration of the mobility of the oxygen molecules in the air. This view, however, had been contested by Wartha, who concluded that it was due to the effect of pressure on the dissociation point of the hydrocarbons burning in the flame; this taking place more rapidly under increased pressure, and therefore liberating the carbon more quickly. However this might be, the effect of pressure on luminous flames was very marked, even under ordinary atmospheric pressure; the difference of an inch in the barometric column making 5 per cent difference in the luminosity. A burner giving 100 units of light with the barometer at 30 inches would only give 95 units if it fell to 29, while a rise to 31 inches would mean an increase of the luminosity to 105 units.

NOTES ON A RED SEDIMENT FORMED IN A RAFFINOSE SOLUTION.

By F. G. WIECHMANN, Ph.D.

WHILE engaged in the isolation of raffinose from a low beet-sugar, the writer incidentally obtained from the raffinose solution a precipitate, bright red in colour, and of peculiar properties, which he has so far been unable to identify as one of the numerous substances whose occurrence in saccharine solutions has been established.

The incident seemed sufficiently curious to merit recording, and although the amount of the substance secured was, unfortunately, too small to permit of ultimate analysis or of an exhaustive investigation, a brief history of the case, and a description of the properties of the body, as far as determined, may prove of interest.

The raw material used for the preparation of the raffinose was an after-product from a German beet-sugar factory employing the strontianite process.

The sugar presented a highly crystalline appearance, and exhibited in profusion the needle formation characteristic of products containing raffinose. In colour it was of a dark brown. The analysis, made in duplicate, showed:—

Polarisation	93.6	93.7
Sucrose	88.2	88.3
Raffinose	2.9	2.9

Work was commenced on November 23, 1888. The different steps taken were as follows:—

To 6000 grms. of raw sugar there were added 6000 c.c. methyl alcohol.

The solution was after some time drained off, and the sugar treated with an additional 4000 c.c. of methyl alcohol.

From the 10,000 c.c. alcohol added, about 7400 c.c. were recovered.

This solution was placed on a water-bath and the alcohol evaporated completely.

When this had been accomplished, and while the solution was still warm, ethyl alcohol was added until a permanent turbidity was caused.

This precipitate was allowed to settle, and was then separated from the clear solution.

This operation was performed six times; the time allowed for settling being in each instance about two days.

Then the raffinose syrup, perfectly free from alcohol, was drawn off.

This syrup amounted to 200 c.c., and was divided into three portions.

As the coloured sediment was produced in only one of these portions, a brief statement of the treatment which each of these portions received is given.

PART I.—20 c.c. were devoted to a trial of Scheibler's method for preparing raffinose.*

Treatment was commenced January 16, 1889, and by September 5, 1889, the separation of the raffinose crystals seemed complete.

PART II.—50 c.c. were treated as follows:—

The specific gravity of the syrup was determined to be 1.4022.

To the 50 c.c. (70.11 grms.), there were added 140.22 grms. acetate of lead. Then absolute ethyl alcohol was added, and the solution heated on a water-bath.

The precipitate which formed was filtered out, suspended in water, and sulphuretted hydrogen was passed in until complete precipitation of the lead had been accomplished.

The sulphide of lead was filtered out and thoroughly washed with water. The filtrate was evaporated on a

* *Zeitschrift des Vereines für Ruben-zucker Industrie*, 1888, p. 337.

water-bath to the consistency of a thick syrup. This was dissolved in very little water, and when cold ethyl alcohol was added, drop by drop, until the turbidity just continued to disappear. The flask into which the solution had been placed was well corked and set aside to allow the crystallisation of its contents. On March 28, 1890, there was considerable of a white crystalline deposit in the bottom of the flask, and the sides of the flask were completely studded with warts of raffinose.

PART III.—On March 28, 1890, work was commenced on the balance of the 200 c.c. previously referred to, and it was in this portion that the coloured sediment was developed.

The specific gravity of the solution was 1.30642. To 97 c.c. of this solution (126.7227 grms.), 253.4455 grms. of acetate of lead were added. Ethyl alcohol was then added and the solution was heated on a water-bath.

This treatment was repeated until all of the raffinose of lead had been precipitated.

This precipitate was then filtered out, suspended in water, and sulphuretted hydrogen gas was passed in until all of the lead had been thrown down.

The sulphide of lead was filtered out and was thoroughly washed with cold water. This was continued until the washings no longer polarised.

To the filtrate blood-carbon of the best quality was added; this was thoroughly shaken up with the solution, allowed to remain in it for about 12 hours, and then filtered off from the then almost colourless liquid. The blood-carbon was then washed with water until the washings no longer polarised.

The washings were added to the filtrate and the whole evaporated at a temperature of about 70° to 75° C., under partial vacuum, to the thickness of a syrup.

This syrup reacted decidedly acid, and upon testing, sulphuric acid was found to be present. This acid was exactly neutralised with barium hydrate, and the precipitate of barium sulphate was filtered out. The filtrate, which was of a light amber colour, was concentrated to a thick syrup by evaporation in partial vacuum.

The solution again turned dark and again reacted slightly acid. Barium hydrate was once more added to neutralisation; an additional quantity of the best blood-carbon was also placed in the liquid, and the whole was allowed to stand at rest for four days.

The solution was then filtered through asbestos, washed slightly with water, and set aside.

It would now have needed only the addition of ethyl alcohol and a leaving at rest to secure the crystallisation of the raffinose.

When set aside the solution was perfectly clear and of a light brownish colour. After allowing it to stand well corked for 24 hours, on close inspection it was found to contain a bright red sediment, in colour not unlike red sealing-wax. On moving the solution the sides of the glass vessel were seen to be coated with a beautiful rose-coloured film.

The solution looked at by transmitted light was of a brownish yellow colour; by reflected light the solution was opaque and of a very dark green colour, resembling in appearance the heavy oils of petroleum; looking across the surface films of emerald-green and rose were visible.

The solution was allowed to stand well corked, and at rest, for seven days, during which period the sediment increased.

At the end of this time the sediment was filtered out, the filtrate being passed into a covered flask in order to avoid exposure to the atmosphere.

This filtration yielded a perfectly clear brownish yellow solution which had lost every trace of fluorescence. This filtrate, well corked, was set aside (June 18th), in order to learn whether any more of the coloured sediment would be developed in it.

This solution will hereafter be referred to as specimen A. The sediment, all of which had been retained by the filter-paper, was of a bright red colour, resembling in tint,

as already stated, ordinary red sealing-wax. By reflected light it exhibited an emerald-green sheen.

This sediment will hereafter be referred to as specimen B.

To remove all raffinose solution adhering to the filter-paper the sediment B was washed moderately with distilled water. The washings were caught and kept in a separate flask.

These washings were preserved for three months and no sediment having formed in them they were then discarded.

The filtrate (A) was inspected from time to time. The following are some of the entries recorded:—

June 18th.—Solution perfectly clear; colour brownish yellow, no fluorescence.

June 19th.—No change.

June 20th.—Distinct though thin layer of sediment has formed, adhering uniformly to all parts of the glass in contact with the liquid.

June 21st.—Sediment slightly increased. A green fluorescence of the solution is noticeable.

June 23rd.—Sediment increasing. Distinct rose layers on sides of vessel. The solution is brownish yellow by transmitted light and dark green by reflected light.

These observations were continued through July and August. The rose-coloured sediment in the solution gradually changed in colour to a rich brown. At the beginning of September it was noticed that white round disks, which seemed to be mould formations, appeared floating on the surface of the solution. Fearing a possible destruction of the coloured precipitate at the bottom of the flask, these disks were removed and the sediment filtered out.

This sediment was marked specimen C.

The solution after the sediment had been filtered out was of a dark brown colour, and without any fluorescence.

It was treated with absolute ethyl alcohol, and after standing a few hours yielded a copious brownish grey precipitate, which should, and probably will, prove to be raffinose. This precipitate, however, yet awaits purification and re-crystallisation from alcohol.

The red sediment first obtained, specimen B, was for months preserved practically unchanged. It was kept on the original filter-paper, of course carefully protected from the dust.

Examined under the microscope with low powers (3.4 and 1.5 objectives with respectively the A, B, and C eyepiece), the substance exhibited an appearance like scales, partly round, partly angular; no crystalline system could be distinguished.

When submitted to examination by a Zeiss immersion lens the sediment was found to consist of small plates and rod-like formations.

It was impossible to determine with certainty whether the rod-like formations were bacteria or of crystalline structure.

The deposit is, however, probably a chemical precipitate. Dr. A. A. Julien, who also kindly examined the specimen, expressed this view, which is strengthened by the following considerations:—

1. The sediment was formed in the liquid, preferably on the sides and bottom of the flask, whereas most chromogenic bacteria are aerobic, and hence would display greatest activity at the surface of the solution.

2. The sediment is insoluble in alcohol, whereas bacteria colours are soluble in this reagent.

3. The rods vary considerably in size, whereas bacteria would exhibit fairly uniform dimensions.

As this coloured sediment was not formed in either of the two preceding portions of the raffinose solution, but only occurred in that portion which was decolourised with blood-carbon, it was natural to suspect that this reagent might have been the source of the sediment in question.

Hæmatin was looked for in a hydrochloric acid solution

by the spectroscope (absorption bands), but with negative result.

Attempts were then made to obtain hæmatin from some of the blood-carbon by treatment with acetic acid and ether. This also failed to yield even a trace of the substance sought.

The supposition that this sediment is hæmatin will, therefore, have to be abandoned, although some of the reactions given further on would point to a body of this nature.

Subjecting the blood-carbon to treatment with twenty times its volume of 75 per cent alcohol, and subsequent addition of barium hydrate—a repetition of the conditions of the experiment, but in the absence of the raffinose syrup—also failed to produce the coloured sediment, thus proving that these reagents alone could not have given rise to its existence.

Various reagents were tried in the attempt to find a solvent for the sediment. It was found to be:—

Soluble in hydrochloric acid, concentrated.

Soluble in nitric acid, concentrated.

Soluble in sulphuric acid, concentrated.

Insoluble in acetic acid, concentrated.

Insoluble in turpentine.

Insoluble in ethyl alcohol.

Insoluble in methyl alcohol.

Insoluble in water.

Insoluble in sucrose solution, concentrated.

Insoluble in ether.

Insoluble in ammoniac hydrate, concentrated.

A test made with a hydrochloric acid solution of the sediment showed it to be inactive to polarised light.

On burning some of the substance on platinum foil a small residue remained; this gave a distinct reaction for iron, an impurity introduced by the barium hydrate which had been used for neutralisation.

Tests made on the hydrochloric acid solution of the sediment proved the presence of barium and iron, and the absence of calcium, potassium, and sodium.

In the absence of data obtained by ultimate analysis it would be idle to speculate on the nature of this substance, remarkable for its fluorescence and brilliant colour. As, however, its properties seem to differ from those of any body known to occur in saccharine solutions, it seems permissible to assume that it is either some substance hitherto entirely unknown, or else a new derivative or compound of raffinose.—*School of Mines Quarterly*, New York, vol. xii., No. 1.

PROCEEDINGS OF SOCIETIES.

FRANKLIN INSTITUTE.

(CHEMICAL SECTION.)

Tuesday, November 19, 1889.

Mr. T. C. PALMER, Vice-President, in the Chair.

THE nomination of officers for the ensuing year was taken up. The following nominations for President were made:—Mr. T. C. Palmer, Prof. S. P. Sadler, Prof. R. L. Chase. On motion, the nominations for President were closed.

Nominations for two Vice-Presidents were then made. The following gentlemen were put in nomination:—Dr. H. H. Keller, Mr. W. L. Rowland, and Prof. Henry Trimble. On motion, the nominations for Vice-Presidents were closed.

Dr. W. C. Day was nominated for Secretary, Dr. H. W. Jayne for Treasurer, and Dr. William H. Wahl for Conservator.

Mr. W. W. McFARLANE gave a description of some new dyeing materials, in which he explained the use of a

number of dyes which have recently been introduced into this country by the representatives of Fried. Bayer and Co., of Elberfeld; samples of dyed products were also exhibited.

Among other interesting matters, the speaker stated that "carmine blue" is dyed with the use of Glauber's salt and sulphuric acid, in the same way as indigo carmine or extract, and further, that the carmine blue will probably displace the indigo extract at no distant period in the future. "Sulphon Azurin" is also used in dyeing cotton, using a boiling bath and some alkaline salt, such as borax, sal-soda, sodium phosphate, or silicate. The blue produced is similar in shade to that of indigo, and is said to withstand the action of light and of dilute acids as well.

Benzo-black-blue is dyed in cotton in the same way as other benzo-colours, and very dark shades are the result. There are two shades of this colour, designated respectively as G and R.

The paper was discussed by Messrs. McFarlane and Palmer.

Dr. WAHL, from whom a paper was expected, announced that he must defer, until a later meeting, his paper on "a new gold-like alloy;" and gave in place of this a statement of further results obtained by him in the electrolytic deposition of platinum, exhibiting specimens of work. As the investigation is not yet entirely completed, and certain details of the mode of procedure are to be made the subject of letters-patent, the speaker preferred, for the present, to withhold the same from publication.

Dr. WAHL also made some critical remarks on statements made in a paper by A. J. Rogers, on "Experimental Researches in the Reduction of the Difficultly-reducible Metals," which was published in the *Proceedings of the Wisconsin Natural History Society*, April, 1889, expressing doubts, based on theoretical considerations, as to the accuracy of one of the results announced by the author; namely, that he had obtained "a yield of aluminium six times greater than had ever been obtained by electrolysis."

Mr. F. LYNWOOD GARRISON presented some remarks on the Paris Exposition, with special reference to Metallurgy and Fuels. As these remarks will be embodied later on in a full and comprehensive report to the Institute, they are omitted here; this paper was followed by a general discussion of some of the statements it included.

Prof. E. F. SMITH read a paper on the "Occurrence of Vanadium in Caustic Potash." This paper was referred for publication. He then presented another on the subject of nitration by the use of nitrogen trioxide as obtained by the action of nitric acid on arsenic trioxide. This paper was also referred for publication.

Professor SMITH next presented the following results of further work in the electrolysis of metallic sulphocyanide solutions. His object in presenting these results was to reserve for the future the field upon which he has entered. In addition to the results already reported in a former paper, it was observed that iron, cobalt, and nickel in sulphocyanide solutions were fully deposited by weak currents, and that the presence of a sulphocyanide in manganese solutions prevented the formation of the dioxide, and when the latter had already precipitated the addition of KCNS would effect its re-solution. To these facts may be added that mercury, cadmium, bismuth, and lead deposit from sulphocyanide solutions. With lead, a behavior analogous to that noted with manganese was observed.

Approximate quantitative separations were made in several cases, but the complete development of these observations requires further study. Another line of experiment has been the electrolysis of metallic phosphates in the presence of free phosphoric acid. Mercury, silver, copper, cadmium, lead, iron, zinc, cobalt, and manganese have given interesting results qualitatively and quantitatively. Separations seem possible when regard is had to the proper condition of the current. The speaker stated

that although in possession of quantitative figures in some of these cases, he preferred to postpone their publication until a careful examination has been made with each metal. Curiously enough, with manganese phosphate dissolved in phosphoric acid there is no separation of dioxide; the solution slowly acquires a red tint, and in time becomes turbid, although the addition of more acid causes the turbidity to disappear.

Dr. Warwick, at the request of Professor Smith, has begun an electrolytic study of the metallic formates; the results obtained will be communicated later.

Tuesday, November 18, 1890.

MR. T. C. PALMER, President, in the Chair.

THE report of the Committee on the Publication of the Paper by Dr. Masser, of Los Angeles, Cal., on "The Curve of the Elements," and also another by Dr. Hans von Strombeck, of New York, on "The Constants of Ammonia" was accepted, and the committee was discharged.

On motion of Dr. WAHL, it was voted that a committee be appointed to prepare a circular-letter addressed to chemists at large, setting forth the facilities possessed by the Section to receive, examine, and publish promptly papers of meritorious character on chemical subjects.

In this circular-letter, he proposed also to call attention to the fact that a number of printed copies of an accepted paper would be returned to the author, within two weeks of the date of its acceptance by the Section; and furthermore to the fact that the publications of the Section are forwarded promptly, as advance sheets, to the leading chemical journals at home and abroad.

The following nominations of officers for the ensuing year were then made:—For President, Dr. Wm. H. Wahl; for Vice-Presidents, Mr. H. Pemberton, Jr., and Dr. Wm. H. Greene: for Secretary and Treasurer, the present incumbents in each case; for Conservator, Dr. Wahl.

Dr. GREENE then presented a paper by himself and Dr. WAHL, on "*Alloys of Sodium and Lead*." It was referred for publication in the *Journal*.

Dr. GREENE also stated that he would submit a number of specimens of new alloys proposed by the authors at the next meeting.

Dr. WAHL then read an abstract prepared by Prof. C. F. Himes, of Carlisle, describing a new photographic process without the use of metallic salts, based on the light sensitive properties of primuline. It was referred for publication. In connection with this paper Mr. Macfarlane stated that the active substance of the process known as "primuline" and the primuline dyes in general had been abandoned in dyeing, because of the fact that they would stand exposure to direct sunlight for only a short time before fading out.

Dr. JAYNE called attention to a chart illustrating clearly the details of the new process for manufacturing nitric acid, invented by Oscar Goodman, and recently described in various journals.

Mr. PALMER exhibited a piece of logwood which was unusual in presenting a bronzy green surface, such as is commonly found only in chipped wood that has been put through the process of curing. This fragment was part of a log six feet in length, taken from a wind-shaken tree through which rain-water had percolated. The rain-water, probably by the action of the ammonia contained it, had produced a result analogous to that secured by the usual curing process.

On Di-isobutylamine Ethyloxalate.—H. Malbot.—The substance obtained has a composition corresponding to the formula $C_{12}H_{25}O_4N$.—*Bull. de la Soc. Chim. de Paris*, Vol. iv., No. 8.

NOTICES OF BOOKS.

Researches on Micro-Organisms: Including an Account of recent Experiments on the Destruction of Microbes in certain Infectious Diseases, Phthisis, &c. By A. B. GRIFFITHS, Ph.D., F.R.S.E., F.C.S., &c. London: Baillière, Tindall, and Cox.

BACTERIA and their doings figure as prominently in our medical literature as ever did the "Solar Myth" in the lucubrations of historians and archaeologists, though with much better reason. The work before us is not a formal manual of bacteriology, but an account of some recent researches in that department, chiefly in connection with infectious diseases. The part played by microbes in the chemistry of agriculture and of fermentation is not overlooked, but forms a less prominent feature.

Dr. Griffiths gives a significant hint in his introduction. "It must not be supposed because the blood and tissues of animals suffering from contagious diseases contain certain microbes that these microbes are necessarily the cause, even indirectly, of the disease. Not until the investigator has obtained by pure cultivations in an artificial sterilised medium, the microbes in a perfectly pure state, and then, by injecting into the blood, &c., of an animal, the disease is reproduced, can one say that a particular disease is the result of the life history of a certain microbe." Thus the physiologists and chemists of Britain, whether they are medical men or not, find themselves practically excluded from this department of research by the deplorable Anti-Vivisection Act.

For bacteriological work the author recommends the microscopes of Zeiss, of Jena. Sterilising appliances are brought into due prominence. Indeed, the student who enters upon such researches will find his attention called at every step to the necessity of sterilisation.

In the classification of microbes we find them arranged as micrococci, bacteria, bacilli, vibriones, spirilla, and spirochætæ, all being now fully recognised as plants. The rate of increase of these beings is truly terrible. A single bacterium will, in the course of a week, have multiplied to a number which can only be expressed by figures of fifty-one places. Hence, ultra-microscopical as they are, we need not wonder at the part which they play in Nature.

The author regards air, water, and soil as means of distributing pathogenic microbes, and human intercourse as a still more powerful factor. It is a painful fact—to which Dr. Griffiths does not refer—that Australia, South Africa, and temperate South America, which once ranked among the healthiest countries of the world, have within the last 25 years acclimatised diphtheria and typhoid fever.

The author admits that flies may convey poison from a diseased to a sound animal. But he scarcely lays sufficient weight on the agency of two-winged insects, including both the blood-suckers and those which merely settle upon man and domestic animals—as the colporteurs of zymotic affections. What is the poison of the Tzetzé?

The remark that moderately high-lying places are particularly liable to the attacks of Oriental plague is perfectly justified by history. In the north of Derbyshire the tourist is even yet shown "the graves of Eyam"—a mountain village which lost practically its entire population in a visitation of the plague.

The author is convinced that the mischief effected by pathogenic microbes is not so much due to their vital activity as to their power of manufacturing poisonous products. Of these substances there are three classes—ptomaines or putrefactive alkaloids; leucomaines, which are produced in health as well as in disease; and "extractives." The latter class, though nitrogenous, are not basic and are incapable of crystallising. One of the authorities quoted makes use of the term "toxic" to express the quantity of any poison capable of killing

1 kilo. of living animal matter. But as different animals are unequally susceptible to the action of different poisons the "toxic" ought to be referred to some one species—say the rabbit.

The properties of many ptomaines are most remarkable. Some of them give off very offensive odours. Others, poisonous all the same, have the fragrance of orange flower, of cinnamon, syringa, the rose, or other flowers.

Probably the most formidable body of this class is hydrocollidine, which is regarded as "nearly as poisonous as the venom of the cobra."

Some of the non-poisonous microbes have the power of forming a variety of pigments from the matter in which they live. Indigo itself is the product of a bacillus, which, however, is pathogenic. *Micrococcus prodigiosus* has been known to appear on bread, which it turned of a blood-red. In the middle ages such phenomena were ascribed to sorcery, and sometimes served as a pretext for the persecution of the Jews.

A very interesting chapter is devoted to the action of heat, light, electricity, gases, &c., on microbia. It is found that certain lower organic forms, both animal and vegetal, can retain their vitality for years; in one case given by Mr. W. Carruthers, F.R.S., of the British Museum, some specimens of *Tylenchus* were re-vivified after they had been in the National Collection for upwards of thirty years.

No species of microbe experimented on by the author was able to resist an electric current of 3·34 volts.

We regret that we are not able to carry further our examination of this most interesting and suggestive work, which deserves our warmest recommendation.

The Physical Properties of Gases. By ARTHUR L. KIMBALL. London: Heinemann.

THIS work is one of the series of Scientific Hand-books now being issued by the publisher. The author, who appears to hold a chair at the "Johns Hopkins" University, here undertakes to give a general view of our present knowledge concerning gases adapted to the requirements of the non-specialist. No attempt is made, of course, to teach anything not fully known and acknowledged in the scientific world, but our present state of knowledge is very fully and clearly expounded.

After an introduction the author discusses pressure and buoyancy, elasticity and expansion with heat, gases and vapours, with a notice of the recent experiments of Caillelet and Piëtet on the liquefaction and solidification of gases; air-pumps and high vacua, under which head we find an illustrated account of the mercurial air-pumps of Geissler and Sprengel; diffusion and occlusion; the thermodynamics of gases; Avogadro's law, and the kinetic theory, and Geissler tubes and radiant matter. The author admits that "the phenomena of the radiant condition of matter as developed by Crookes, furnish, perhaps, the strongest experimental evidence of the truth of the kinetic theory of gases in its essential features."

In a concluding chapter the author quotes the opinions of the late Clerk Maxwell, against the formation of the various kinds of molecules by evolution. None of the arguments brought forward, however, seem conclusive, and we may venture to think that if Professor Maxwell had lived to follow the results of recent experiments, e.g. on the rare earths, he would have modified his opinions.

Although this book has been printed in England, we regret to see that the American orthography has been adopted. Thus potassium nitrate is spoken of as "niter." If so, why not on the same principle write "possibel," &c.? There is no foot-hold between our ordinary English orthography with all its anomalies and the wholesale innovations of the "Fonetic Nuz."

In a general preface to the entire series of works, for which Mr. Kimball is evidently not responsible, we find a very objectionable expression.

The writer aims at explaining "the most important inventions and practical discoveries of the present day." This is part and parcel of that confusion between art and science against which we, in common with not a few men of wider influence, have all along protested. An invention always is or aims at being "practical," whether for good or evil.

A discovery cannot be practical; it is simply the announcement of some truth, old as Creation, but hitherto overlooked.

The atomic theory, the periodic law, the persistence of energy are discoveries; photography, the telephone, the spectroscope are inventions.

The man of culture who wishes for a general and accurate acquaintance with the physical properties of gases will find in Mr. Kimball's work just what he requires. We hope we are within measurable distance of the time when such knowledge will be demanded as imperatively as classical lore has been in the past.

A Systematic Handbook of Volumetric Analysis; or the Quantitative Estimation of Chemical Substances by Measure Applied to Liquids, Solids, and Gases. By FRANCIS SUTTON, F.I.C., F.C.S. Sixth Edition, enlarged and improved. London: J. and A. Churchill.

THIS work evidently increases at once in bulk and in value, and certainly holds its place in the estimation of chemists.

A few points only, and those of subordinate interest, seem to call for remark. Looking over the table of abbreviations we regret to find that gramme is contracted into "gram," which, if not carefully written, may easily be mistaken for grain. Nor do we see what is to be gained by writing "liter," "centimeter," &c.

Heretical as it may seem, we cannot help doubting whether chemists have not been too precipitate in abandoning the so-called "empirical" standard solutions which express the proportion of a constituent at once in percentages without any calculation. This advantage will, to many persons, more than compensate for the trouble of keeping a greater variety of standard solutions.

On the subject of normal solutions there is unfortunately no small confusion. The author, like Mohr, Fresenius, and Classen, follows the equivalent system. Pattison Muir in his version of Fleischer's *Maassanalyse*, and Muter in his "Manual of Analytical Chemistry" seem to be inconsistent.

The analysis of water is explained at great length, especially as far as the Frankland and Armstrong process is concerned. The microscopical and cultural examination is of course only slightly touched upon as not strictly belonging to the subject of the work.

CORRESPONDENCE.

OUTLINES OF GENERAL CHEMISTRY.

To the Editor of the Chemical News.

SIR,—To-day I received the last number of your valuable journal, containing the favourable account of my little book.

In your commencement you give a quotation from my preface, which contains just the opposite to my meaning; for I have not written "the necessity of the employment of higher mathematics," but "the necessity of avoiding the employment," &c.

Further, I have expressly stated that the understanding even of the new development of chemistry is possible without higher mathematics; only for useful work in this branch it is indispensable. I am quite aware that there

exist broad districts in chemistry, where great discoveries can be made without this most useful means.

W. OSTWALD.

December 21, 1890.

[The passage on which our comments were founded is in the Author's Preface (English translation), lines seven to five from bottom:—"that the reader who has only an acquaintance with elementary mathematics may be brought to see the necessity of acquiring at least the rudiments of the higher analysis."—Ed. C. N.]

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—We have striven in our letters on this subject on the 28th ult. and 12th inst., to be, above all things, plain in our statements. It appears, however, that we have failed to be sufficiently explicit for certain correspondents who seem scarcely to have grasped the ideas we endeavoured to convey.

"A Contributor to the *Journal of the Chemical Society*" deprecates the "Chemical Society of London advertising itself." Such deprecation cannot but command sympathy; it is, however, to be feared that the word "advertise" has been understood in its modern and limited sense, and that the phrase "advertise itself" has been considered equivalent to "indulge in self-laudation." A re-perusal of our last letter will probably suffice to dissipate this idea and to restore the Society's equanimity by leading to the withdrawal of the threat of resignation, under which it has doubtless quailed.

We will ask you to accord us a little further space in which to reply to Mr. Friswell, who has hinged a second protest from himself upon our last letter.

We were not aware that we had any "difficulties" in the matter; in our first letter we asserted that we believe the Chemical Society to be in a dilemma, in our second we stated what appear to us the only possible issues therefrom.

The Society is certainly not responsible for the erroneous tendency of the public to confer a professional status upon its members, but to accept passively the advantages accruing from that tendency is scarcely consistent with self-respect. Nor will the charter serve as a refuge; such a crisis was not foreseen fifty years back, and charters are not unalterable.

We have never recommended *wild* black-balling under any circumstances; we have never even advocated the *vigorous* black-balling mentioned in the first alternative set forth in our last letter, merely indicating it to be a logical necessity for those who adopted that alternative. We asserted that *all* or *no* candidates must be admitted while this question is *sub judice*, because we were fully conscious both of the incapacity of a meeting (as at present constituted) of the Chemical Society to act in any sense as a qualifying body, and of the invidious distinctions that would be—we had almost said, were being—made by those scarcely qualified to judge.

The present system will undoubtedly be sufficient if those who uphold it will take steps to rectify the public estimate of the value of the letters F.C.S.; otherwise we repeat that they will convict themselves of being either illogical or dishonest.—We are, &c.,

A. G. BLOXAM.
BERTRAM BLOUNT.

ALLOYS OF SODIUM AND LEAD.

To the Editor of the Chemical News.

SIR,—The report of Messrs. Greene and Wahl's paper on "Alloys of Sodium and Lead" given in last week's *CHEMICAL NEWS* contains wrong densities for certain

mixtures of those metals. By calculation a mixture containing 10 per cent of sodium has a density 10.36, one containing 19.5 per cent a density 9.36, and one containing 31.7 per cent a density 8.1. The authors give the respective densities of such mixtures as 5.6, 3.7, and 2.7, figures which it is difficult to see how they obtain. If the observed densities of the alloys are given correctly, they are considerably lower than those of mixtures of the same composition, not higher as is stated in the paper.—I am, &c.,

W. J. A. B.

December 27, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

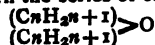
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 24, December 15, 1890.

On the Detection and the Determination of Very Small Quantities of Aluminium and Cast-Iron in Cast-Irons and Steels.—Adolphe Carnot.—Aluminium has been used of late in some works to impart to cast-irons and steels special properties which are particularly appreciated in casting. Its introduction, even in very small proportions, appears to exert a great influence; but its manner of action has not yet been properly determined, and we do not know with certainty if a part of the aluminium exists in the state of an alloy in the cast-iron or the steel, or if it disappears entirely in the state of oxide, though still preventing the formation of carbon monoxide and the production of blow-holes in the metal. For the thorough study of this question it is necessary that metallurgists should possess an accurate and simple method of analysis, enabling them to recognise and determine very small quantities of aluminium in iron. He purposes here to make known a method which he uses and which he has taught for eight years at the Paris School of Mines. His researches date back to July, 1882; they were undertaken at the request of M. Lan, then Professor of Metallurgy at the School of Mines. He considered that the presence of minute quantities of aluminium or of the alkaline earthy metals might have a great influence on the quality of cast-metal, of iron, and steel. He sent the writer specimens of cast-irons from the different works of the Châtillon-Commentry Company, with the request to determine the small quantities of aluminium, which he suspected might be present in some of them, obtained from the very aluminiferous ores of Berry. The results of the analyses were almost absolutely negative for the cast-irons, in which there were found only doubtful traces of alumina, which might be due to small inclosed particles of slag. Such researches had then merely a theoretical interest, and the author had neglected to publish them. Since that time aluminium has been purposely introduced into irons and steels intended for casting, and the question of the determination of this metal thus acquired a greater importance. The method in question is founded upon reactions which the author pointed out in the *Comptes Rendus*, July 18, 1881, May 8, 1882, and April 7, 1884. The alumina may be completely precipitated as a neutral phosphate on boiling in a slightly acetic liquid. This precipitation succeeds equally well in presence of a considerable quantity of iron, which is not thrown down if the precaution has been taken of reducing the ferric salt to the ferrous state by means of sodium thiosulphate. The author takes about 10 grms. of the metal, and treats it with hydrochloric acid in a platinum capsule. He avoids, as far as possible, the use of glass or porcelain vessels to prevent the accidental introduction of alumina from this source. When the

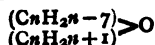
metal is entirely dissolved without allowing the solution to become peroxidised in the air, it is diluted with distilled water and put in a flask or a beaker of Bohemian glass, washing several times by decantation, and retaining the insoluble matter, such as silica and graphite, upon a filter. A small quantity of silica may remain in solution, and must be eliminated subsequently, but it is convenient not to make this elimination at the outset by evaporating the solution to dryness, as an excessive quantity of ferrous salt is present. The bulk of the free acid is then neutralised with ammonia and then with sodium carbonate. Sodium thiosulphate is then added. When the violet colour has disappeared, and there no longer remains any ferric salt in the colourless solution, there are added 2 to 3 c.c. of a saturated solution of sodium phosphate and about 20 c.c. of a solution of sodium acetate. The mixture is then heated to ebullition, which is kept up for about forty-five minutes as long as the slightest odour of sulphurous acid is perceptible. There is formed a precipitate, generally not bulky, of aluminium phosphate mixed with sulphur and containing a little ferric phosphate. This precipitate is collected on a filter, washed with a little boiling water, and then placed over a platinum capsule and treated in heat with 10—15 c.c. of hydrochloric acid diluted with water. The solution is evaporated to dryness, and the residue is kept at 100° for one hour, so that the silica may become entirely insoluble in acids. The residue is then taken up in a little dilute hydrochloric acid, which dissolves all the aluminium and iron phosphates. The liquid is then filtered to remove silica, diluted with 100 c.c. of cold water, and the precipitation is repeated in the same manner as before, *i.e.*, almost complete neutralisation with sodium carbonate, addition (in the cold) of thiosulphate, and subsequently of a mixture previously prepared of 2 grms. acetate and an equal weight of thiosulphate, boiling for half an hour, and filtration through a small paper filter which has been washed with acids and which leaves no ash. The silica and any iron which remained in the first precipitate are thus completely eliminated from the second, which after washing with boiling water is dried, ignited, and weighed. The aluminium phosphate thus obtained contains 22.45 per cent of alumina.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iv., No. 10.

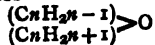
Researches on Dispersion in Organic Compounds (Ether Oxides).—Ph. Barbier and L. Roux.—The specific dispersive powers of the alcoholic oxides are of the same order of magnitude as those of the alcohols from which they are derived. In the series of oxides—



the dispersive powers vary regularly with the molecular weights and increase with them. In the series of oxides—



they decrease regularly as the molecular weights increase. In the series of oxides—



the specific dispersive powers have a value which is approximately constant in the different terms of the series. The specific dispersive powers of isomeric compounds are sensibly the same, and the addition of CH₂ in the molecule occasions a variation of the specific molecular dispersive power equal to about 8. Lastly, the specific molecular dispersive power of an alcoholic oxide is equal to the algebraic sum of the specific molecular dispersive powers of its components.

Researches on Dispersion in Organic Compounds (Fatty Acids).—Ph. Barbier and Roux.—The specific dispersive powers of these bodies increase regularly with the molecular weights. The specific dispersive powers of

isomeric compounds are nearly the same, those of the abnormal acids being slightly inferior to those of the corresponding normal acids. The introduction of CH₂ into the molecule occasions a variation of the specific molecular dispersive power, which is constant for the different terms of the series, and is about equal to 7.8.

Essays on the Laws of Berthollet.—A. Colson.—The author proposes to apply these laws to the alkaloids.

Action of Hydrofluoric Acid upon Diastase.—Dr. Effront.—The author has stated that hydrofluoric acid acts more energetically than the other mineral acids upon the lactic and butyric ferments. The temperature is most favourable to fermentation, but much lower.

Action of Isopropyl Iodide upon Aqueous Ammonia in Equimolecular Proportions at 100°.—H. and A. Malbot.—The principal products of the reaction are di-isopropylamine and propylene.

Action of Isopropyl Chloride upon Aqueous Ammonia in Equimolecular Proportions at 140°.—H. and A. Malbot.—There is formation of mono- and di-isopropylamine, partly free and partly combined.

General Process for the Synthesis of the β-Acetonie Ethers.—L. Bouveault.—Not adapted for useful abstraction.

Action of Phenylhydrazine upon the β-Ketonic Nitriles.—L. Bouveault.—It may be said that the tertiary β-acetonie nitriles yield with phenylhydrazine true hydrazides, whilst the secondary β-ketonic nitriles produce amidopyrazols.

MISCELLANEOUS.

Recovery of Uranium Residues.—Laube (Zeit. Angewandte Chemie) recommends a modification of the Reichardt process. The residues from titrations are collected together, and the clear liquid is decanted off from time to time. When a sufficient quantity has been collected the pasty mass is either heated in the pot by introducing steam, or in an iron pan over an open fire. Soda crystals are then added until the precipitate appears chiefly dissolved. It is let cool, mixed with a sufficiency of ammonia, and the phosphoric acid is precipitated with magnesia mixture. After standing for 12 hours the supernatant liquid is syphoned off, and the precipitate is washed with ammoniacal water. The alkaline liquids are neutralised either with hydrochloric or sulphuric acid, heated to expel carbonic acid, and the uranium is precipitated at a boiling heat with ammonia as uranium oxide ammonium. The precipitate is washed by decantation. A small quantity of some ammonium salt must be added to the last washing-waters, as the precipitate otherwise does not settle well. For obtaining uranium nitrate the precipitate is dissolved in excess of nitric acid and concentrated by evaporation.

Detection and Determination of Yolk of Egg.—S. Bein (Berichte der Deutsch. Chem. Gesellschaft).—The colouring-matters of egg yolk are exposed to changes on exposure to the air which render its identification in articles of food practically impossible. In particular Thudichum's reaction (a blue colouration with nitric acid) cannot be obtained. The author founds a process for the determination of yolk upon the determination of the phosphorus present in the substances which are extracted by ether, especially the glycerin phosphoric acid and the lecithine. He makes an ethereal extract of the substance in question, evaporates and incinerates at a gentle heat with the addition of a little saltpetre, and obtains in the ash the phosphorus which was present in the glycerin phosphoric acid and in the lecithine. By operating cautiously so as not to destroy the lecithine 1.2502 grms. of phosphoric acid obtained in the ash proves the presence of 100 grms. yolk of egg.

Messrs. Dunn and Co.—This old-established business has been purchased by Mr. Thomas Tyrer, of the firm of Messrs. May and Baker, of Battersea, now dissolved. The business will be continued under the title of Thomas Tyrer and Co., Stirling Chemical Works, Stratford, E.

The Clothworkers' Technical Scholarship.—This valuable scholarship (value £240) has again been taken by a pupil (aged 13) of the St. Thomas Charterhouse Schools. Notwithstanding the competition for this great prize becoming keener year by year, so far this school produces the winner. The subjects of Examination were mathematics, drawing, science, and the usual English subjects.

A Contribution to the Valuation of Zinc Powder.—G. Klemp.—Of the numerous methods proposed for ascertaining the value of zinc powder, the only one which has come into general use is that of Drewsen, depending on the reductive action of metallic zinc in an acid solution. The author shows that the results of this method are discordant and too low. In all the methods proposed the presence of lead or iron must interfere with the results. The author has sought for a method permitting the determination of the metallic zinc in zinc powder by ascertaining its reductive power in alkaline solutions. After having tried potassium ferricyanide in an alkaline solution unsuccessfully he took up potassium iodate, which is converted by reducing agents into the corresponding iodide. If potassium iodate is used in excess on acidifying the solution, iodine is liberated, the quantity of which bears a definite proportion to the metallic zinc contained in the zinc powder used. 15 Zn correspond to 6 I and 0.1 grm. Zn to 0.407799 I or to 0.1356 grm. KIO_3 and 0.086 KOH. In ascertaining the conditions of the reaction, he finds that if dilute lye is used, and in theoretical quantities, only the decomposition of the zinc powder is slow and imperfect. If a more concentrated solution is used, and in greater quantity, the decomposition is more complete and more rapid. If no excess of potassium iodate is present hydrogen escapes. The solution of the zinc powder is accelerated by shaking up with glass beads or other bodies having a comminative power. In order to absorb the hydrogen evolved the potassium iodate and the zinc powder must be intimately mixed, which can be effected only by the use of strong solutions of potassium iodate; but the concentration must be such that when mixed with concentrated potassa lye there is no separation of potassium iodate. Zinc powder is also decomposed by water, although slowly; hence in quantitative determinations the zinc powder should be placed in dry vessels. The solution used in the author's experiments contained 15.25 grms. KIO_3 in 300 c.c.. In quantitative determinations the author used 0.1 grm. zinc powder, 3 c.c. of the iodate solution; the total quantity of liquid (solution of potassium iodate, potassa-lye, and any water added) was 13 c.c. to each 0.1 grm. of zinc powder. The determination of the iodine set free is effected by distillation in the Töpfer apparatus, the iodine being received in a solution of potassium iodide. The solution obtained is titrated with a solution of sodium thiosulphate containing per litre 7 grms. $\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O}$. For titrating back there is used a dilute solution of iodine, of which 2 or more c.c. corresponded to 1 c.c. of the solution of thiosulphate. The author suggests that aluminium may be determined in the same manner, and proposes to examine the subject further.—*Zeitschr. f. Analyt. Chemie*, Vol. xxix., Part 3.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Chloride of Magnesium.—Can any one recommend me to a book or paper that treats on the manufacture of chloride of magnesium?—W. H. B.

MEETINGS FOR THE WEEK.

MONDAY, 5th.—Medical, 8.30.
Society of Chemical Industry, 8. "The Basic Copper Process," by Percy Gilchrist. "On Standard Sperm Candles," by W. C. Young.
TUESDAY, 6th.—Pathological, 8.30.
Royal Institution, 8. "Frost and Fire," by Prof. Dewar, M.A., F.R.S.
WEDNESDAY, 7th.—Geological, 8.
THURSDAY, 8th.—Royal Institution, 8. "Frost and Fire," by Prof. Dewar, M.A., F.R.S.
Royal, 4.30.
Royal Society Club, 6.30.
Mathematical, 8.
FRIDAY, 9th.—Astronomical, 8.

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THE CHEMICAL NEWS.

VOL. LXIII. No. 1624.

ON THE SO-CALLED II., OR COMPOUND SPECTRUM OF HYDROGEN ACCORDING TO DR. B. HASSELBERG, AND ON THE STRUCTURE OF HYDROGEN.

By Prof. A. GRUNWALD.

THE author has continued the investigation of the second hydrogen spectrum observed by Dr. R. Hasselberg.

Whilst he formerly confined himself to "Balmer Series" of at most four members (wave-lengths): $\lambda_1, \lambda_2, \lambda_3, \lambda_4$, and was only able to resolve a part of the hydrogen spectrum of Hasselberg into such series, it now appeared, on extending the consideration to more than 4 members, that with 8 members almost the entire spectrum can be divided into groups whose corresponding wave-lengths, $\lambda_1, \lambda_2, \dots, \lambda_8$ from Balmer series.

The author understands by a "Balmer series of n members" a series of n wave-lengths, $\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_n$, two of which at least belong to the compound hydrogen spectrum, and for which the proportions hold good—

$$\frac{1}{\lambda_1} : \frac{1}{\lambda_2} : \frac{1}{\lambda_3} : \frac{1}{\lambda_4} : \dots : \frac{1}{\lambda_n} = 1 - \frac{4}{3^2} : 1 - \frac{4}{4^2} : \dots : 1 - \frac{4}{(n+2)^2}$$

where one value of the magnitude independent of n corresponds to each single series of this kind.

The author has collocated these series and the corresponding mean values of h in an especial table, which we cannot insert here.

Not all the wave-lengths belonging to any given wave-length can be found in the spectrum given by Hasselberg. The gaps which thus occur are due in part to the circumstance that the missing wave-lengths do not fall within the region of the spectrum observed by Hasselberg ($\lambda = 6422.67$ to $\lambda = 4412.0$ of 1883, or the additional spectrum $\lambda = 4497.35$ to $\lambda 4062.07$ of 1884), but in part because the electric illumination of the hydrogen contained no rays capable of exciting the vibrations in question with the necessary intensity.

From the above it follows in consequence of the author's theory, and of dynamic-chemical considerations otherwise known, "that the molecule which radiates out the II. or compound hydrogen spectrum consists of two equal secondary atoms H, each of which possesses a stratified structure, and consists of a nucleus of maximum density with a series of forms of condensation of one and the same primary matter "a" surrounding it in strata, or possibly in the form of a ring, and of densities diminishing progressively outwards. If we suppose the nucleus with the immediately surrounding strata, exclusive of the v outermost = $r(v)$ (where v is one of the whole numbers 1, 2, 3, 4), and if we designate the last v strata, or rings, which represent the same number of primary chemical atoms "a" in determinate forms of condensation from the outermost stratum towards the nucleus respectively with $a^{(1)}, a^{(2)}, a^{(3)}, a^{(4)} \dots a^{(v)}$, then—

$H = a^{(1)}, a^{(2)}, a^{(3)}, a^{(4)}, \dots, a^{(v)}, r(v)$ ($v = 1, 2, 3, 4$), the general chemical formula for the simple secondary hydrogen atom H, which according as we put $v = 1$ or $= 2$ or $= 3$ or $= 4$, &c., assumes different special forms. Especially if we put $v = 4$ and $r^{(4)} = b$, we have—

$H = a^{(1)}, a^{(2)}, (a^{(3)})^2, a^{(4)}, b$, or more briefly, $H = a_4 b$.

In other words, the so-called simple hydrogen atom H can be conceived as a compound similar to ammonium

H_4N of an atom "b" with four primary atoms "a" in the different condensations $a^{(1)}, a^{(2)}, a^{(3)}, a^{(4)}$.

The atom "b," which in the author's earlier memoirs was supposed to be quite independent of the primary atom "a," appears now in the light of the most recent results as exceedingly complex, consisting of a nucleus surrounded by strata, all capable of being derived from the primary element "a," so that this seems to be the true "protyle." It becomes at the same time very probable that the remaining chemical atoms, so-called, such as K, Na, &c., are single atoms or systems of single atoms in the stricter sense, each of which possesses a stratified structure resembling that of the simple hydrogen atom, the structural elements of which (nucleus and strata, or possibly rings), can be derived according to a fixed law from the primary atom "a." Thus the atom "a" discovered by the author, and the group of the values of h deduced by him from Hasselberg's hydrogen spectrum, which are simply the wave-lengths of protyle in a certain form of condensation which he names the "central," acquire an extraordinary importance for an understanding of the structure of all the derived chemical elements.—(Reprinted from the *Anzeiger*, No. 19, of the Imperial Academy of Sciences at Vienna).

SEPARATION OF BARYTA, STRONTIA, AND LIME.

By A. RUSSMANN.

THE author has subjected a number of the methods proposed for this purpose to a critical examination, the results of which he communicates in an elaborate memoir.

1. *Method of Frerichs*.—Russmann experimented first with this method, precipitating a pure solution of barium with neutral potassium chromate after an addition of acetic acid and ammonium acetate, letting settle completely, filtering, washing with dilute acetic acid, drying at 110° , and weighing. The results were approximately accurate, but though a trace of barium could be detected in the filtrate the amount found was in excess of the truth, as the precipitate always contained small quantities of potassium chromate.

In using this method for the separation of barium and strontium attempts were made to separate varying quantities of strontium from a constant quantity of barium. Russmann took into account the advice of Meschezeraki, that the saline solutions should be diluted to 0.5 to 1 per cent. From the experiments it appears that in solutions which contain to 50 parts of barium 20 to at most 15 parts of strontium no strontium is precipitated. In solutions containing relatively larger proportions of strontium appreciable quantities of it are carried down along with the barium chromate.

In separating baryta and lime the quantity of the latter does not interfere, as calcium chromate is not precipitated.

In order to dispense with the use of a weighed filter the author attempted to determine the barium chromate by weighing the precipitate after ignition in a porcelain crucible. The precipitate was first removed from the filter as completely as possible, the portion adhering to the paper was dissolved in dilute nitric acid, the solution evaporated down in the tared crucible, and the main quantity of the precipitate then added. The result was not satisfactory, as portions of chromic oxide were formed by the action of the fibres of the paper.

Russmann also endeavoured to determine barium volumetrically by decomposing the barium chromate with hydrochloric acid and potassium chromate. Experiments of this kind performed in various manners gave results in excess, as the hydrochloric acid of itself liberated iodine from the potassium iodide. The best results were obtained in the simplest manner by dissolving the precipitate of barium chromate in dilute hydrochloric acid,

mixing the solution with potassium iodide, and titrating with sodium thiosulphate immediately after dilution.

C. Diehl's Method (*Journ. Prakt. Chemie*).—According to this method a mixture of barium sulphate and calcium sulphate recently precipitated is gently heated repeatedly with a concentrated solution of sodium thiosulphate. The calcium sulphate dissolves, and may be determined with ammonium oxalate, whilst the barium sulphate remains undissolved. Russmann could not obtain accurate results. There always appeared a deficiency of lime, as the barium sulphate retains calcium sulphate, the error becoming more considerable as the proportion of lime is greater. If it is intended to determine the calcium in the filtrate the sodium thiosulphate must first be decomposed by boiling with hydrochloric acid.

The sulphur thus eliminated involves a further source of error, as it incloses small quantities of lime. If we attempt to avoid the separation of sulphur and add to the dilute solution of sodium thiosulphate containing the lime ammonia prior to evaporation, sulphur is still deposited on the dry parts of the capsule, and on precipitating the lime with ammonium oxalate this finely divided sulphate accompanies the precipitate, and on ignition converts a part of the lime into sulphate. The method cannot be recommended on account of the inconvenience and tediousness of repeatedly treating the sulphates with sodium thiosulphate.

Separation of Barium and Calcium by Means of Sulphuric Acid.—This method can be successfully used both in solutions in which small quantities of barium exist along with much calcium, and in such as contain part calcium to 100 parts barium. On using 10 to 20 c.c. hydrochloric acid containing 25·28 HCl, lime never accompanies the precipitate. In very dilute solutions the method certainly requires much time, as the precipitate is not completely deposited within twenty-four hours.

Method of D. Sidersky.—A neutral solution of strontium and calcium compounds being mixed at a boiling heat with the dissolved mixture of ammonium sulphate and oxalate gives a precipitate of strontium sulphate and calcium oxalate. These salts are separated either by treating the filtered precipitate with dilute hydrochloric acid, which dissolves the lime salt, or by mixing the solution at the outset with hydrochloric acid, which keeps the lime salt from being thrown down.

Experiments conducted in the former manner showed that on washing the precipitate with dissolved hydrochloric acid considerable quantities of the strontium sulphate passed into solution, and the time when all the lime is removed from the precipitate cannot be determined. In this form the method is not applicable even for technical purposes.

As regards the second method of execution Russmann concludes that if a very dilute acid is used a little calcium oxalate easily accompanies the strontium sulphate. If a stronger acid is used a part of the strontium sulphate is dissolved. Approximate results may be obtained by working in such a manner that the liquid on precipitation contains at least 8·4266 per cent of hydrochloric acid. For separating barium and calcium the method of Sidersky is applicable.

Method of C. H. Bloxam (See CHEMICAL NEWS, vol. liv, pp. 16 and 168).—On examining this method Russmann arrived at the conclusion that it is very well adapted for the detection of small quantities of calcium in presence of much strontium, as 1 part of calcium can be recognised along with 500 parts of strontium. But the quantitative determination of lime by means of ammonia and arsenic acid presents more difficulties than its determination as calcium oxalate, since in the latter method there is no need for a weighed filter. Besides, the results, although only 20 per cent calcium instead of 20·86 were supposed to exist in the precipitate dried at 100°, are not such as can be recommended.

On attempting to render the precipitate fit for weighing

as $\text{Ca}_2\text{As}_2\text{O}_7$ after ignition a considerable loss of arsenic could not be avoided even with special precautions.

The method cannot be used for the quantitative separation of strontium and calcium, since calcium sulphate on precipitation carries down considerable quantities of calcium; the results are fluctuating and very unfavourable.—*Zeitschrift für Analytische Chemie*.

(To be continued).

NOTES ON KJELDAHL'S PROCESS.

By VINCENT EDWARDS, F.O.S.

MANURE works' chemists are so frequently called upon to estimate nitrogen in such substances as dried blood, shoddy, fleshings, soot, &c., of more or less value that it becomes a matter of importance to have some accurate and reliable yet not too costly method within reach. The old soda-lime process is of course a very good one, and comparatively simple, but the chief difficulty is the gas supply, which is not always powerful enough if it exists at all. I have known some works without it. As to the ancient plan of red-hot charcoal, which is still recommended by some chemists of the "old school," I consider it as much out of place as the rack and thumb-screws would be in a court of justice. As the following modification of the apparatus usually said to be required for Kjeldahl's process may be useful to those who work in somewhat isolated places, I venture to submit it.

The digestion of the substance, 1 grm. for ordinary manure, 0·5 grm. for guano and rich substances, I carry out in the manner recommended in the CHEMICAL NEWS, vol. lix, No. 1525, except that rather less oxide of mercury will answer; about 0·2 grm. is enough. For description see the same CHEMICAL NEWS. Messrs. Mawson and Swan will supply them. The flasks can be supported in any convenient manner over a rose burner, and nothing hardly will break them. A spirit lamp will answer if there is no gas, but the time required will be much longer.

I think the pictures of apparatus given in some books are rather discouraging, as not only are they very elaborate but next to impossible to procure. Very simple forms of condenser and receiver will answer just as well as a metal one; in fact too much condensation delays the process and is entirely unnecessary. I use a 500 c.c. flask on a sand bath, with a rubber cork, through which passes a tube which is carried about three inches into a small tubulated retort holding about 110 c.c. (this quantity of distillate will contain all the ammonia); the stopper of the retort is replaced by a cork, through which passes the bent end of a Will and Varrentrap's nitrogen bulb tube; this contains the standard sulphuric acid, drawn in as usual from a beaker, into which at the end of the operation the whole distillate, acid in bulbs, &c., are emptied. For titration with normal soda diluted to 1 in 3. This may seem a very simple apparatus, but I can confidently assert it will answer as well as many costing five times as much. Certain precautions are necessary with these modifications—the heating of the distilling flask must be gradual and carefully done as the alkali is apt to spray at first; the gas must not pass too quickly through the Will and Varrentrap bulb tube. In fact an eye must be kept on the whole concern during the process. The chemical details will be found in the paper I have mentioned. 35 grms. of caustic soda can be dissolved in 60 c.c. of water; if it is not desirable to make a quantity of saturated solution this is enough, if 20 c.c. of strong acid is used for the digestion. I think a Florence oil flask would answer for this if the others are not at hand. A glass tube about a foot long and 1½ inch in diameter will do very well for a condenser; there is a cork at each end through which the tubes pass, and which retains the water; this can be run off when it is almost boiling, and cold or moderately warm water run in without fear of breaking

the glass or stopping the process. A little ingenuity will enable the analyst to construct a condenser out of appliances which are always at hand.

Dublin, Dec. 26, 1890.

ON GASEOUS ILLUMINANTS.*

By Professor VIVIAN B. LEWES.

II.

In the second Cantor Lecture on the above subject, Professor Lewes pointed out that, in the various analyses of illuminating gases, the heavy hydrocarbons are, as a rule, expressed as "illuminants," and were formerly considered to consist mainly of ethylene. This is an idea which the researches of the last few years have shown to be totally erroneous, as, besides ethylene, there is undoubtedly present benzene, propylene, butylene, and acetylene, and probably such members of the paraffin series as ethane, propane, and butane, while under certain circumstances, crotonylene, terene, allylene, and others, are present. The determination of the illuminants is therefore by no means the simple process one would imagine it to be from the directions given in most text-books on gas analysis.

The illuminants present in any given sample of coal gas depend upon (1) the kind of coal used, (2) the temperature at which it is distilled, and (3) the length of time the gas is in contact with the heated sides of the retort, as well as with the liquid products of the distillation.

Having dealt with this part of the subject at considerable length, the lecturer then went on to consider the methods of analysis which can be utilised in determining the constituents of an illuminating gas, and showed that all analyses of coal gas have hitherto been founded on the idea that the "illuminants"—i.e., the heavy hydrocarbons responsible for the illuminating power—could be absorbed by fuming sulphuric acid, chlorine, or bromine. This, however, he said, is undoubtedly not the case. Mr. Wright has shown that, when coal gas has been treated with this acid, the residual gas still retains from 32 to 55 per cent of its original luminosity; and although this may, to a certain extent, be owing to the methane, which at high temperature becomes slightly luminous, it is certain that a considerable percentage is due to the higher members of the paraffin series which are not absorbed by the acid, and which the methods of analysis usually employed utterly fail to detect. Indeed, given a gas containing any member of the paraffin series other than methane, the analytical results are not only incorrect, but misleading, as the percentages of hydrogen and methane present will be absolutely nullified by a very small quantity of the higher hydrocarbons.

The processes instituted by Bunsen, and used with all forms of mercury apparatus, have several drawbacks; the chief one being that the residue left after absorption with Nordhausen acid was looked upon as hydrogen, methane, and nitrogen, and that these were estimated by explosion with oxygen, and the volume of carbon dioxide formed was taken as representing the volume of methane. All researches on the composition of coal gas point to the presence of ethane, and probably of higher members of the marsh gas series; while in carburetted gases they are undoubtedly present to a far higher extent. Ethane, propane, and butane have all been shown to be present in small quantities; and as ethane gives double, propane three times, and butane four times its own volume of carbon dioxide, it is evident that exploding with oxygen and taking the volume of carbon dioxide as representing marsh gas will undoubtedly give too high results with ordinary coal gas, while with a carburetted gas it will render the whole analysis useless.

Moreover, the free oxygen is next absorbed, and the remainder taken as nitrogen; and the volume of gas after absorption by Nordhausen acid, less the marsh gas and nitrogen, is taken as representing the hydrogen in the gas. The result is that the hydrogen is always far too low, not only because the volume of marsh gas is too high, but because the residual nitrogen, having to bear the brunt of all the errors of analysis throughout some seven or eight absorptions, is also nearly always too high. These palpable errors in the quantity of marsh gas and hydrogen also render worthless the calculations of carbon and hydrogen density of the gas, on which great stress has been laid by previous observers. On the whole, therefore, it is not to be wondered at that no relation has been discovered between the carbon and hydrogen density and the illuminating value of the coal gas. With the more rapid methods of technical analysis, it is evident that no explosion over water, and subsequent measurements of carbon dioxide, could give satisfactory or even approximate results, as the pressure at the moment of explosion, and the subsequent reduction of pressure, cause the water to effervesce like soda water from the absorption, and then the liberation of the carbon dioxide; and as this washes out other gases dissolved in the water, leaving an indefinite quantity of carbon dioxide in solution, any such process must be discarded.

These troubles have induced chemists to suggest several modifications in the process, some of which aim at doing away altogether with explosion. Certain of these, like the process of burning hydrogen, but not methane by passage over palladium asbestos, are of great value. The last method proposed for the analysis of coal gas without explosion has been published this year. It consists in absorbing the illuminants by strong alcohol, the carbon dioxide by potash, the oxygen by pyrogallate of potash, the carbon monoxide by cuprous chloride, the hydrogen by alkaline solution of permanganate of potash—calling the residual gas methane and nitrogen. The objections to this process are that alcohol not only absorbs the illuminants, but also a very large percentage—say, 50 per cent—of the methane, with considerable rapidity; that, after washing with water from the alcohol vapours, it would be useless to expect an exact determination of the carbon dioxide, as it has been mostly dissolved; and finally that, as far as Professor Lewes' experiments have at present gone, alkaline permanganate is not a reliable absorbent for hydrogen. He is now working at the various processes of gas analysis, and checking the several methods by the analysis of known mixtures of pure hydrocarbon—work which he expects to have ready for publication early next year. So far, the general scheme of analysis which he is following, and which gives him the best and most instructive results, is as follows.

Two of Stead's apparatus are taken and placed with the entrance tubes end to end, and filled—one with distilled water saturated with air, and the other with clean pure mercury. The gas to be tested is collected in one of the Stead absorbing tubes, over water, so as to be saturated; it is then transferred over mercury in the eudiometer-tube of the second apparatus, and measured and passed into sodic hydrate, in order to absorb the small trace of carbon dioxide to be found in the highly-purified London gas. When present in only small traces, the amount of carbon dioxide lost by water saturation cannot be detected, while a calculation is avoided. After the absorption of the carbon dioxide, the gas is run into the second apparatus, and the oxygen estimated by absorption with alkaline pyrogallate, which must be strong and fresh, containing about 25 grammes of pyrogallallic acid dissolved in 50 grammes of sodic hydrate in 200 c.c. of water. It is absolutely essential that the solution should be fresh, as after some time it will evolve a considerable amount of carbon monoxide. The heavy hydrocarbons have now to be estimated; and inasmuch as benzene is one of the most valuable illuminants in the coal gas, it would be of great value if any absorbent could be found that would

* Abstract of the Cantor Lectures delivered at the Society of Arts. Communicated by the Author.

separate the benzene and ethylene series. Unfortunately this does not exist as far as is known; the usual absorbents having the following drawbacks: (1) Nordhausen sulphuric acid, in which sulphur trioxide has been dissolved until it will solidify on cooling, absorbs both ethylene and benzene, and therefore cannot be used to separate them. (2) Fuming nitric acid is a good absorbent for both series. (3) Bromine water acts far more rapidly on ethylene than on benzene, but undoubtedly does absorb a considerable quantity of the latter if left long in contact with a mixture of the two. (4) None of the foregoing affect methane in diffused daylight. The nearest approximate result is obtained by treating the gas first with strong bromine water, but not leaving it too long in contact with it, and then removing bromine vapour over sodic hydrate—the absorption being taken as the ethylene series; while the benzene is absorbed by fuming nitric acid or saturated Nordhausen acid—acid fumes being removed in the sodic hydrate tube before measurement over water. After absorption with nitric acid gas, it is run back into the eudiometer, and measured over water. It is then passed into an absorption-tube filled with a fresh solution of ammoniacal cuprous chloride. This must not be used for more than six determinations of an ordinary coal gas containing (say) 3 to 6 per cent of carbon monoxide or three of a carburetted water gas, as after much carbon monoxide has been absorbed, the solution has a tendency to again give up small quantities of the gas.

The gas is now returned to the mercury eudiometer-tube; and, after measurement, it is passed into an absorption-tube containing ordinary paraffin oil (previously heated until everything that will distil at 100° C. has gone off), which absorbs ethane, propane, butane, and a good deal of the methane. The residue is then washed and mixed with oxygen, which has itself been analysed, so that the percentage of nitrogen and foreign gases in it are known, and the mixture exploded over mercury. The carbon dioxide formed is estimated; and its volume *plus* the volume of gas absorbed by the paraffin gives the volume of gases in the methane series. A fresh portion of gas is now taken over mercury, and is exploded with excess of analysed oxygen. The carbon dioxide is absorbed by sodic hydrate and the oxygen by pyrogallate; and the residue will be the nitrogen—the hydrogen being determined by difference. In this way an analysis of South Metropolitan gas shows—

Illuminants	Hydrogen	47.9	Total Hydrocarbons
	Ethylene series	3.5	
	Benzene " } approx.	0.9	
	Methane series { by paraffin	7.9	
	{ by explosion	33.3	
		45.6 p.c.	
	Carbon monoxide	6.0	
	Carbon dioxide	0.0	
	Oxygen	0.5	
	Nitrogen	0.0	
		100.0	

In such an analysis, the lecturer remarked, no pretence was made that the exact percentage of each illuminant was given. But the total of the hydrocarbons were accurate, and their rough subdivision gave a far clearer insight into the characters of the gas than the more pretentious and more faulty analysis upon which it has been customary to argue. He said it must be clearly borne in mind that he only put forward this scheme of analysis to meet the need now rapidly arising for a method which would show whether ordinary coal gas enriched by canal coal gas carburetted with either gasoline or oil gas, or coal gas enriched by highly carburetted water gas, was being dealt with. In the first case the ethylene and benzene series would be found well represented, while the carbon monoxide was low; in the second, the amount of hydrocarbons in the methane series would have become greater; and if oil gas had been used a small increase in carbon monoxide might also be noticed, while the presence

of carburetted water gas at once brought up the quantity of carbon monoxide, and the methane series became more important illuminants.

Professor Lewes went on to show that the light-giving value of the hydrocarbons present in coal gas vary very greatly; the illuminating power increasing very rapidly with the number of carbon atoms in the molecule.

The action of the diluents in coal gas upon its illuminating power has been determined by Dr. Percy Frankland by taking ethylene, with its illuminating value of 68.5 candles, as representing the hydrocarbons in the gas, and diluting with the various diluents present.

The results show that, with the combustible diluents, hydrogen reduces the illuminating power least with large quantities of the hydrocarbons; but that marsh gas is preferable when in excess, as with low percentages of the illuminant, especially when burnt at a high temperature, marsh gas itself becomes a feeble illuminating agent. This is due to the fact that although, when the marsh gas or methane burns at ordinary temperatures, it is non-luminous, at a high temperature some of it is broken up into acetylene, which gives it distinct luminosity. Carbon monoxide is the most injurious of the combustible diluents, 80 per cent mixed with ethylene rendering it non-luminous—a result which would require 90 per cent of hydrogen to bring about.

The influence of incombustible diluents on the illuminating power of flames containing hydrocarbons has been also determined.

Moisture, when present to the extent of 2 per cent (the proportion present in coal gas saturated at 20° C. and 760 m.m.), with ethylene, reduces the illuminating power 3.6 per cent, or in coal gas 3.3 per cent. Of the inert or non-combustible diluents, therefore, carbon dioxide is the most injurious, while atmospheric air is the least harmful. Wurtz has also determined the loss of light incidental to the addition of air to coal gas, and he gives the following results:—

Added Air.	Percentage Loss of Light.
3'00	15'69
4'96	23'83
11'71	41'46
16'18	57'53
25'00	84'00

The addition of oxygen to gases rich in hydrocarbons causes an increase in the illuminating power up to a certain point, by raising the temperature of the flame, by burning up the hydrogen of the hydrocarbons, and rendering the carbon incandescent, without diluting the flame with nitrogen to the extent that would have been necessary had air been used for the purpose. The effect of such gases as hydrogen, marsh gas, and carbon monoxide is simply to dilute the flame, and, by separating the molecules of the hydrocarbons, to make them more difficult to decompose; whereas such bodies as carbon dioxide, nitrogen, air, and water vapour not only dilute, but also cool the flame, as they do not add to the heat by any action of their own, and have to be heated up to the same temperature as the flame itself. Rosette determined the temperature of a gas-flame diluted with air, nitrogen, and carbon dioxide respectively, and found that it was least with the last-named gas, and highest with air—a result which agrees with Dr. Frankland's determination of illuminating power. His figures are as follows:—

Volumes taken.			Temperature.		
Gas.	Diluent.	Air.	Nitrogen.	Carbon dioxide.	
1 vol.	1 vol.	..	1180° C.	..	1100° C.
1 "	2 "	..	1260° C.	..	880° C.
1 "	3 "	..	1116° C.	..	780° C.

Preservation of Flexible Tubing (*Pharm. Zeit. für Russland*).—The author places the coils of tubing in water containing a little salt.

A NEW METHOD OF MAKING ALLOYS.*

By WILLIAM HALLOCK.

WHILE occupied with a careful study of an article by W. Spring† on the production of Wood's alloy, and seeking the forces possibly brought to bear in his experiments, the following explanation occurred to me, and was subsequently verified by critical experiments. The method of production used by Mr. Spring was to mix filings of the four metals in the proper proportions, subject the mass to a pressure of 6000 atmospheres, file up the block thus produced and compress it a second time, obtaining as an end result a block of Wood's alloy.

Now, if at any time during the various operations, be it the first compression, the subsequent filing, or the second compression, or if anywhere in the whole mass the original metals came in contact all together, then at that point we should have a particle, a molecule as it were, of Wood's alloy. If thereafter the temperature ever rose to 70° C., that particle would melt and dissolve down its immediate neighbours until finally the whole mass was liquefied and converted into a homogeneous mass of alloy. Without waiting to consider how improbable it was that the three or four metals could be brought simultaneously into perfect enough contact to act as a real alloy, I tried the experiment and it proved an easy success.

The metals were filed to fine grains and mixed in the proper proportions, one part cadmium, one part tin, two parts lead, and four parts bismuth. A glass tube of 5 m.m. inner diameter and 70 m.m. length, sealed at one end, served as containing vessel. About 6 grms. of the mixed filings were placed in this tube and packed down, an iron wire 3 m.m. diameter, held between the thumb and finger, being used as a packer; which certainly eliminated the possibility of any considerable pressure. The tube was thereupon so placed upon the water-bath that the sealed end containing the metals projected downward into the boiling water. In this way the filings remained dry and were kept at a temperature of 98° to 100° C. After remaining in this position for eighteen hours (over night) the filings showed signs of sinking together, which would indicate a beginning of the reaction. The tube was jarred upon the table to assist the condensation and again placed on the bath. Two hours later the tube contained a *homogeneous liquid globule of Wood's alloy*. The experiment was repeated, using two larger tubes, into which the metals were packed with a lead pencil, and producing some 30 grms. of alloy. Of course when the operation is once started there is no limit to the quantity which can be produced. One tube remained on the water-bath over a week without signs of a solution and yet finally dissolved.

In further application of the same principle lead and tin were melted together at 190° to 200° C. by simply laying a piece of tin upon a carefully cleaned piece of lead and placing the whole in an air-bath at 190° C. A few hours suffice for this experiment. The melting points of the above metals are—Cadmium 315° C., tin 230° C., bismuth 267° C., lead 325° C. Potassium and sodium were also used, melting at 62° 5' C. and 95° 6' C. respectively.

A very interesting and striking experiment is the production of the alloy of equal parts of potassium and sodium, which is liquid at temperatures above 6° C. Pieces of the two metals are simply placed with freshly cut surfaces in contact and slightly pressed together; in a few seconds the liquid alloy, which resembles mercury, is visible in drops around the contact surface, and an hour or two suffices to produce several cubic centimetres of the fluid.

It is my intention in the near future to follow up these observations by a series of experiments intended to establish and extend the principle here illustrated. The

heat phenomena which doubtless accompany these reactions will also be investigated. Possibly also some electrical manifestations may be discovered, and perhaps some facts bearing upon the origin of contact electricity may be developed. In the meantime I would propose the following law:—An alloy can be produced out of its original constituents without considerable pressure if the temperature be above the melting point of the alloy, even though it be far below the melting point of the most easily fusible constituent.

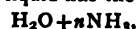
Probably this law will also be found applicable wherever under the existing circumstances the product is a liquid, even though the original substances be solids.—*Bulletin of the United States Geological Survey*, No. 60.

COEFFICIENTS OF VOLATILITY FOR AQUEOUS CHLORHYDRIC ACID.

By ROBERT B. WARDER.

THE various questions of physical chemistry are claiming more and more attention, and problems relating to states of aggregation seem to have a special interest. The art of fractional distillation on a manufacturing scale has developed a great variety of appliances, but much remains to place the theory on a satisfactory mathematical basis, especially in the case of bodies which exert a mutual affinity.

The term "coefficient of volatility" was introduced by Wanklyn* to indicate the relative readiness of different constituents to volatilise. Thus he found that when a very dilute solution of ammonia was distilled until 1/10 of the water passed over, nearly 1/2 of the ammonia had distilled with it. He estimated that a given quantity of water in any small fraction of the distillate was accompanied by 13 to 14 times as much ammonia as the same quantity of water in the boiling liquid. Expressed more formally, if a boiling liquid has the composition—



and yields a mixed vapour represented by $H_2O + v n NH_3$, the factor v is the coefficient of volatility, and in the case cited v equals about 13 or 14. Since this gas may be absorbed in indefinite proportions, of course the coefficients n and $v n$ may be fractional, indicating the number of molecules of NH_3 divided by the number of molecules of H_2O .

In the case of chlorhydric acid, as is well known, when the liquid boils under the ordinary atmospheric pressure, it tends to acquire the constant composition $HCl + 8H_2O$, or $H_2O + 1/8 HCl$. After a stronger or weaker acid has reached this composition, on further boiling $n = v n$ and the factor $v = \text{unity}$.

The well-known researches of Roscoe and Dittmar† showed that an acid of higher composition will boil unchanged under diminished pressure; a similar result was observed upon evaporation in a current of air of given temperature to supplement the partial pressure exerted by acid and aqueous vapour. Hence it is clear that v depends not only upon the composition of the mixture, but also upon the pressure (or temperature) at which the distillation is conducted. The published data relate to the conditions under which $v = 1$, but no attempt has yet been made to show the relation between v and n .

The more recent researches of Roozeboom show certain conditions of equilibrium among solid, liquid, and gaseous phases of aqueous chlorhydric acid‡ and other compounds which are illustrated by thermodynamical theory; § but

* *Philos. Magazine*, [4] 45, 129 (1873). *Pharm. J. Trans.*, [3] 3, 543 (1873).

† *Jour. Chem. Soc.*, 12, 128.

‡ *Rec. Trav. Chim. Pays-Bas*, 3, 84 (1884). Abstract in *Zeitsch. physik. Chem.*, 1, 365 (1887), and 2, 459 (1888).

§ *Rec. Trav. Chim. Pays-Bas*, 5, 335, (1886). Abstract in *Zeitsch. physik. Chem.*, 2, 462 (1888).

* Read before the Philosophical Society of Washington, D.C., at the meeting of February 28, 1888.

† W. Spring, *Ber. der Chem. Gesell.*, vol. 15, 1882, pp. 595–597.

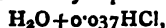
the papers do not discuss the ordinary conditions of distillation.

Many operations of manufacturing, geological, and analytical chemistry depend upon the partial or complete separation of volatile constituents. Chlorhydric acid is typical of a large number of substances which have strong attraction for the solvent; and a more exact knowledge of its volatility as a function of the composition is the object of this research.

Experimental Method.

One hundred cubic centimetres of chlorhydric acid of known strength was subjected to fractional distillation in a boiling flask of 250 c.m.³ capacity. Successive portions of the distillate were conducted through a Liebig condenser and discharged near the bottom of receivers; a loosely fitting cork was used to hinder evaporation. The several fractions, after weighing in well stoppered vessels, were titrated with sodium hydrate, containing a little barium hydrate and carefully protected from the air by soda lime. Phenolphthalein was used as indicator. In some cases very weak distillates were evaporated with excess of ammonia, and titrated with centinormal silver solution and potassium chromate. The water was determined by deducting the acid from the total weight of the fraction. As a rule no reliance was placed upon specific gravity, the ordinary summer temperature of the room being far above that recognised in the tables; hence, the acid used for each distillation was weighed. The residues in the boiling flask were also weighed and titrated for control.

When fractional distillation is conducted for the purpose of separating the constituents, this is promoted by some kind of dephlegmation; this may be accomplished by exceedingly simple means, as the walls of an ordinary boiling flask, by the complicated appliances of the manufacturers, or by the many devices for laboratory use. The object of the present work required the exclusion of dephlegmation, since this would introduce an element of great uncertainty. The flask was placed in a cylindrical air bath and covered with a conical hood of sheet copper. By means of a ring burner (as devised by Gibbs), with very gentle air blast, a circle of gas jets was thrown upon the copper cone, so as to keep the upper part of the flask heated far above the boiling point of the fluid, while distillation was effected by a large Bunsen burner under the air bath. A thermometer in the vapour was usually kept at a temperature of 145° to 153°. The boiling point of the liquid was from 100° to 109° C. (varying with the concentration); and from the rate of distillation and the space above the liquid, it was estimated that the vapour would pass from the surface to the condenser in about six seconds; hence it is not to be supposed that the thermometer indicated the actual temperature of the vapour, but something between this and the temperature of the radiating surface of glass or copper. By this means the condensation of moisture upon the sides of the flask was prevented. In a preliminary experiment with



the first fifty per cent distilled without the hood and ring burner contained no more acid than the 10 per cent distilled with the precaution described; and this was only one-twentieth as much acid as distilled in the first 50 per cent under the heated cover.

As the distillation proceeded and the volume of vapour increased the temperature had to be moderated by turning down the flame.

In the distillation of strong acid each receiver was weighed with 10 c.m.³ water, to absorb the acid fumes.

Calculation of Results.

The weight of HCl found in each fraction of the distillate subtracted from the total weight leaves the weight of water; and the weights of water and acid thus found in each fraction were subtracted successively from the water

and acid taken to find the composition after the removal of this fraction. The mean composition of the boiling liquid during the removal of each fraction was expressed in the form $\text{H}_2\text{O} + n\text{HCl}$, the composition of the distillate being $\text{H}_2\text{O} + n'\text{HCl}$ or $\text{H}_2\text{O} + v n\text{HCl}$. The coefficient v was then found by dividing n' by n . Four distillations gave 25 pairs of values as follows:—

I.		II.		III.		IV.	
n	v	n	v	n	v	n	v
0.0952	0.284	0.0681	0.140	0.0666	0.084	0.1939	5.44
0.1031	0.423	0.0759	0.194	0.0693	0.111	0.1853	3.71
0.1107	0.537	0.0862	0.282	0.0730	0.158	0.1713	2.40
0.1186	0.645	0.0984	0.429	0.0769	0.172	0.1567	1.66
0.1231	0.868	0.1107	0.597	0.0806	0.198	0.1474	1.31
				0.0844	0.243		
				0.0879	0.247		
				0.0911	0.253		
				0.0944	0.300		
				0.0970	0.311		

Discussion of Results.

Two points remain to be considered:—

First. What formula will best express the values found for v as function of n ?

Second. Do the relations here determined point to actual equilibrium between liquid and vapour?

No one equation was found to express all the values given above. When dilute acid ($n=0.07$ to 0.11) was boiled rapidly (about one grm. per minute) the results agreed with the equation $v=4.45n^2$ as in series II. When strong acid ($n=0.15$ to 0.20) was boiled rapidly, the values of v were somewhat greater than would be indicated by the equation above; approximately, $v=3063n^2$, as in series IV. These two empirical curves, which occupy different parts of the field, are entirely consistent with each other, but must be regarded as a *first approximation only* to the function sought. When the dilute acid of Series I. and III. was boiled from 20 to 60 per cent more slowly than that of Series II., the values of v were about 10 to 30 per cent less than those indicated by the equation. There can be little doubt that v is a function of the rate of boiling as well as of the composition of the liquid. The problem appears to be dynamical, not a question of equilibrium merely, and I hope to investigate this point further.—*Bulletin of the United States Geological Survey*, No. 60.

AN IMPROVED METHOD FOR THE ESTIMATION OF THEINE IN TEAS.

By G. L. SPENCER.

THE estimation of theine has received considerably more attention from analysts than the value of a knowledge of its proportion in teas seems to warrant. The estimation of the percentage of theine in a tea gives little if any information in regard to the commercial value of the latter, though, in general, it may be said the high-priced teas usually contain a large proportion of this alkaloid.

Twenty-five or more methods have been devised for the estimation of theine, though it must be said the later of these methods bear a strong resemblance to one another. In the earlier methods the alkaloid was extracted from the tea leaves by means of ether or acidulated water, the extract purified, and the theine separated by crystallisation from concentrated solutions, or if finally obtained in ether or chloroform solution, by the complete evaporation of solvent. The various methods differ more especially in the purification of the solutions of the alkaloid.

In the method of Blyth the alkaloid is obtained quantitatively directly from the powdered leaves and in a state of great purity, by sublimation. Some of the later methods differ from one another only in slight variations in the

manipulations, the object being the reduction of the labour required.

Weyrich (*Ztschr. anal. Chem.*, xii., 104) examined a number of theine methods and rejected all but that of Mulder. His objections to the various methods were based upon either imperfect extraction of the alkaloid, imperfect precipitation, or an impure product. The method of Mulder, which he adopted, consists in evaporating a definite volume of a water extract of the tea with magnesia to dryness; the residue is then digested two days with ether; this latter is occasionally heated and poured off into a tared flask, a fresh portion of the solvent being added. This extraction is continued as long as the residue yields theine. The ether solutions are united, and finally the solvent is removed as usual by evaporation. This is a favourite one of the older methods, and is given to emphasize the simplicity of manipulation required by the method, which I propose to describe below. While the method about to be described is but little shorter than some of the new methods, which it resembles, it has the advantage of very considerable accuracy. This method may be briefly described as follows:—

Transfer three grms. of very finely powdered tea to a 300 c.c. flask; fill the flask with hot water nearly to the neck; add a small fragment of tallow to prevent foaming; heat gradually to ebullition, and maintain this temperature half an hour. Small particles of tea adhering to the neck of the flask should be washed down with a few drops of water. After boiling, cool and add subacetate of lead in slight excess. The amount of the reagent required may be determined by the ease with which the precipitate separates. Approximately 0.3 c.c. concentrated lead solution is required per gm. of tea. After the addition of the lead, complete the volume to 300 c.c. and shake the flask to mix its contents thoroughly; filter off 100 c.c. of the solution into a sugar flask, i.e., a flask graduated to 100 and 110 c.c.; precipitate the excess of lead with hydrosulphuric acid, employing ether to prevent foaming; heat to expel excess of the reagent, cool, and complete the volume to 110 c.c. The extra 10 c.c. permits washing the gas delivery tube. Filter, transfer 55 c.c. of the filtrate, corresponding to 0.5 gm. of tea, to a separatory funnel, and extract seven times with chloroform. The chloroform solution of the theine is collected in a tared flask and the solvent removed by distillation and drying. The temperature at which the latter is accomplished should not exceed 79° C. The theine obtained is very pure and contains one molecule of water of crystallisation.

It may be noticed in the above method that all washings of precipitates is avoided. A slight error is introduced through the non-removal of the tea residue and the lead precipitate, but this will rarely if ever exceed about 0.02 per cent. A second error results from leaving the lead sulphide in the sugar flask, but this is extremely small, if care has been taken in adding the lead subacetate. If preferred, the lead may be removed without the use of the sugar flask, a definite volume of the solution being taken for this purpose. In this case the precipitate requires washing. It is preferable to follow the method as first described, as in this way the volume of the solution in the funnel will not exceed 55 c.c., a large volume being objectionable through the possibility of a portion of the alkaloid remaining in water solution.—*Journal of Analytical Chemistry*, Vol. iv., Part 4.

ON THE METHODS OF ESTIMATION OF THE FATTY BODIES IN VEGETABLE ORGANISMS.

By WALTER MAXWELL.

THESE investigations have been conducted with the purpose of acquiring some further data showing the comparative proportions of matters which become separated from vegetable organisms by extracting with pure ether in

variable durations of time. It has further been attempted to determine whether the whole of the substituted glycerides, or lecithines, do become separated by direct extraction with ether only.

The materials used in the work were pulverised to the greatest state of fineness, and the extractions were made with the Knorr extraction apparatus. The calculations are reduced to the standard of water-free material.

a. The preliminary experiments, which were made in order to establish the proportions of the vegetable matters separated by the action of pure ether in different durations of time, are illustrated by the following results:—

Cotton-seed. Time.	Wt. of Material. Grms.	Wt. of Extra. Grms.	Per cent.
8½ hrs.	4	1.472	37.39
10 "	4	1.491	37.87
15 "	4	1.511	38.38

These results give the average of a great number of analyses. Although an increase of substance becomes separated with an increased duration of the period of extraction, the proportion is small; and it is not apparent that the greater duration of time causes an increase in the fatty bodies only, as other matters can be affected by a very protracted boiling. For these reasons it has been resolved to estimate the amounts of the fatty bodies separated by extraction with pure ether in a duration of 15 hours.

In considering the estimation of the proportion of glycerides and substituted glycerides which are contained in the ether extract, the presence of other bodies, which have been removed with the ether, make it impossible, in the absence of an absolute analysis of the extract, to determine accurately the comparative relations of those fatty bodies. The ether extractions of plant matters contain variable proportions of cholesterol and of, in some instances, solid hydrocarbons, which may constitute several per cent of the extract. However, although the percentage of glycerides cannot be definitely estimated, the lecithines or substituted glycerides may be determined with absolute accuracy, as the estimation of these bodies rests upon the proportion of phosphorus present in the ether extract. The extract is ignited with mixed alkali salts, by which the phosphorus present in the organic form as lecithine becomes fixed as an alkali phosphate and is then determined as magnesium pyrophosphate, and the latter body being multiplied with the known Hoppe-Seyler factor, gives the exact amount of lecithine.

A further series of extractions was made of the pulverised cotton-seed with pure ether for a period of 15 hours and the total extract determined. The proportion of lecithine contained in the extract was estimated by the method already given, the residue of the extract being considered as glycerides and other bodies. The average of eight analyses gave the following results:—

Per cent of extract		38.46
Per cent glycerides, &c.		98.84
Per cent lecithines		1.16

b. It will be shown that the proportion of substituted glycerides stated, 1.16 per cent, does not represent the total lecithines present in the cotton-seed.

The observation was made simultaneously by Prof. E. Shulze, Zurich, and W. Maxwell, of Harvard College, that the substituted glycerides do not become wholly separated by extraction with ether, even in a great duration of time. It was found that if the material which had been already extracted with ether were further extracted with absolute alcohol, another portion of substituted glycerides was obtained, which, in most instances, was greater than the amount separated by the ether. The process of the alcohol extraction consisted in merely extracting the material already treated with ether and evaporating off the alcohol, and re-extracting the alcohol extract residue with ether. The reason for taking up the lecithines out of the alcohol extract was that it has been observed that

those lecithines which were originally insoluble in ether became soluble in that menstruum when previously acted upon by alcohol. The use of ether was further made to avoid any small portion of inorganic phosphates which might have been removed from the vegetable material by alcohol. It was found, however, that only a mere trace of mineral phosphates had been separated by the action of the alcohol.

The amount of the ether extraction of the alcohol extract in 100 parts of the vegetable material with the proportion of lecithines was as follows:—

Extract	2.3 per cent
Lecithines in extract ..	16.6 "

A further comparison indicates the following:—

	Extract. Per cent.	Lecithines. Per cent.	Glycerides, &c. Per cent.
Ether	38.46	1.16	98.84
Ether and alcohol	40.76	2.30	97.69

The proportion of lecithines to the total fatty bodies contained in the cotton-seed is very small, yet it is seen that about 50 per cent of those substituted glycerides are left in the material after extraction with ether for a period of 15 hours. If certain other varieties of seeds be considered, such as the legumes, pea, vetch, bean, Boston bean, &c., it is found that the total ether and alcohol extracts of those seeds are composed of lecithines varying from 25 to 45 per cent. It is thus apparent that, in the examples of seeds given, as far as 20 per cent to 25 per cent of the total fatty bodies can remain unseparated and undetermined when the material is extracted with ether only.—*Journal of Analytical Chemistry*, Vol. iv., Part 4.

THE ANALYSIS OF CUPRIC BROMIDE, AND THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

THE uncertainty of knowledge regarding the atomic weight of copper, owing to the widely different values assigned by various experimenters, led nearly four years ago to the beginning of an investigation, of which this paper is the third publication. The two earlier papers (*Proceedings of the American Academy of Arts and Sciences*, xxii., 342, and xxiii., 177; also *Fresenius's Zeitschrift*, xxviii., 392) described a number of determinations made by a method which had not until then been successfully applied,—the precipitation of metallic silver from neutral silver solutions by means of metallic copper. The results obtained were in themselves very satisfactory, but differed entirely from the value which has hitherto been accepted with little question by chemists; and the desire to discover, if possible, the cause of this discrepancy has finally led to the continuance of the investigation.

It is well known that we can rarely find with regard to any element more than one or two compounds which answer the exacting requirements of atomic weight determination; although others of its definite compounds may by their analysis more or less strongly support the verdict of the more exact results. Disagreement implies constant error in one or other of the disagreeing values, and the detection and correction of this constant error can alone give certainty to our conclusions. Much, however, may be learnt by careful study from a new standpoint, and the first step in the present investigation was to discover if possible such an opening.

The basic tendency of cupric salts, and the ready oxidation of cuprous compounds, complicate to such an extent the relations of copper, that the preparation of any one of its salts in a dry state of perfect purity may be

regarded as almost an impossibility. One by one the usual cupric and cuprous compounds were rejected as unsuitable for the foundation of a new research, until finally, after much study, cupric bromide was selected on account of the simplicity and exactness of its analysis, and moreover because by establishing beyond doubt the relation of copper to bromine we connect its atomic weight with precise values previously determined in this laboratory.

The balance used throughout the research was the one used by Professor Cooke in his admirable work upon the atomic weight of antimony, and was kindly loaned by him for the present purpose. A long-armed balance of the best type, manufactured by Becker, of New York, it was very perceptibly turned by one-twentieth of a m.grm. with a load of fifty grms. in each pan, and showed unusual constancy in its indications. It was kept in a large quiet room of nearly constant temperature, and was protected from unequal heating and from air currents by suitable curtains. The weights were made by Sartorius in Göttingen, the larger ones being of gold-plated brass, and the fractions of a grm. of platinum. Three days were spent in their comparison, according to a method somewhat similar to that described by Crookes (*Fresenius's Zeitschrift*, vi., 431), and the very small corrections thus found were tabulated and applied to all results.

Before weighing, every object was allowed to remain in a desiccator near the balance for at least seven hours. Every weight was determined at least thrice, each time according to a different method of swinging, and all precautions for accuracy were taken which are usual in such work. In the first experiments the weighings were made by substitution, but the conditions were so uniformly constant and the balance so manifestly reliable that this procedure seemed a useless expenditure of time. In fact, the probable error of the ordinary method of weighing under such circumstances is very much less than other possible errors of an investigation like the present. It is certain that the total inaccuracy of any weighing, due to all possible causes combined, could not have exceeded seven or eight one-hundredths of a m.grm., and was without doubt usually very much less than that quantity. All weighings were, of course, reduced to a vacuum standard, allowing for the air displaced by the weights. Since these were standardised with reference to a brass ten-grm. piece, it is evident that the fractions of a grm. must be calculated as brass, and not as platinum.

I. PRELIMINARY WORK.

Preparation and Analysis of Hydrobromic Acid.

The next step taken was the preparation of hydrobromic acid pure enough to serve as the basis of research. The acid was made from pure potassic bromide and sulphuric acid, according to the method recommended by Dr. Squibb (*Proceedings of the American Academy of Arts and Sciences*, xvii., 30). It was then purified by repeated fractional distillation, at first in a large platinum retort, and afterward in one of glass, it having been ascertained that the gold used as a solder in the former apparatus was attacked during the process. It was subsequently found that the action of the acid even upon glass was not imperceptible, but as the same retort was used in all later distillations, and as the glass was of good quality, this unavoidable cause of impurity was reduced to a minimum.

The acid was distilled in all ten times,—seven times over potassic bromide, twice over silver bromide, and once alone,—each time the first and last portions of the distillate being rejected. A specimen of the wholly colourless product was preserved for over a year without perceptible change.

The necessity of testing the purity of this hydrobromic acid led at once to the next step of the investigation, the preparation of chemically pure silver. Fused argentic nitrate was first made from pure silver which had been

* Contributions from the Chemical Laboratory of Harvard College.
—From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxv.

reduced from the chloride by milk-sugar and potash. This salt was then dissolved in a large amount of water, and again decomposed by the gradual addition of very dilute hydrochloric acid in slight excess, the precipitate being thoroughly agitated and washed by decantation with dilute hydrochloric acid and hot and cold water. After drying and pulverising, the pure argentic chloride was digested for six hours with aqua regia, and then again washed with the purest hot and cold water until the filtrate gave no test for chlorine.

The final reduction of the cream-coloured product was accomplished as before, by warming it with a dilute solution of the purest caustic potash and milk-sugar, which had previously been filtered through a Gooch crucible. Careful testing showed the completion of the reaction, and the resulting pure silver, having been thoroughly washed with dilute sulphuric acid and a very large amount of pure hot water until perfectly clean, was collected and dried upon a quantitative filter. Small portions of the powder were successively supported upon a carbon dish similar to that described by Professor Cooke (*Proceedings of the American Academy of Arts and Sciences*, xvii., 17), and, after being fused by means of a blowpipe directed downwards, the silver was allowed to cool in a reducing flame. The buttons were hammered upon a clean anvil, scrubbed with sand, rolled out between two plates of pure silver, cut with a hard steel chisel, boiled successively with hydrochloric acid and ammonia, scrubbed once more with sand, and, after heating with melted potassic hydrate in a silver crucible, finally scrubbed, washed, and dried.

In order to prove the absence of any absorbed gases in the resulting metal the following experiments were made:—

- I. 1.3412 grms. of silver heated in vacuo to a low red heat weighed after cooling 1.3412 grms.
- II. 1.5763 grms. after being subjected to the same treatment weighed 1.5763 grms.

The absolute constancy of these weights is sufficient proof of the point in question. The silver yielded a perfectly clear solution upon treatment with nitric acid and subsequent addition of water, and gave every evidence of being chemically pure.

In order to determine the purity of the hydrobromic acid previously made, the solution of a known weight of the pure silver described above was decomposed by a slight excess of this liquid, and the resulting precipitate was weighed. The metal was dissolved in a very slight excess of warm pure nitric acid diluted with two volumes of water, the whole being contained in the half-litre Erlenmeyer flask, which was afterward to serve for the precipitation. The very small amount of gas formed by the decomposition of the nitric acid was forced to pass through a zigzag tube provided with bulbs, in order that the infinitesimal amount of spray might be retained. The tube apparatus was not ground into the flask, but fitted only with moderate tightness, the joint being sealed by water held in place by capillary attraction. After the complete solution of the silver, the contents of the flask were gently boiled to drive off the lower oxides of nitrogen, and the whole was diluted to about two hundred cubic centimetres. To this hot liquid was added very gradually the least possible excess of a dilute solution of known strength made from the hydrobromic acid above described, and the mixture was constantly and violently shaken, the flask being closed with a smooth rubber stopper. After settling, the precipitate was thoroughly washed with hot water, and collected in a Gooch perforated crucible with all possible care. The crucible with its contents was dried at 130° to constant weight, and showed no loss in any case on additional heating to 180°.

The above variation is not greater than a possible error in the operations concerned, and the testimony which these results give to the purity of the materials is sufficient for the present purpose. Other experimenters in

SYNTHESIS OF ARGENTIC BROMIDE.

No. of Experiment.	Silver taken (reduced to vacuum). Grms.	AgBr formed (reduced to vacuum). Grms.	Percentage Ag in AgBr.
1	1.11235	1.93630	57.447
2	1.57620	2.74335	57.455
3	2.16670	3.77170	57.446

Average 57.449
According to Stas 57.445

this laboratory have obtained values ranging from 57.442 to 57.450.

Preparation of Cupric Bromide.

The salt used in the preliminary series of experiments upon the atomic weight of copper was formed by the solution of the purest obtainable cupric oxide in the hydrobromic acid which has been described above. For the preparation of the oxide of copper pure electrolytic metal (of the quality used in the experiments published three years ago) was converted into sulphate by means of pure nitric and sulphuric acids, and the resulting salt was purified by six fractional re-crystallisations after the expulsion of the remaining nitric acid by heat. From a dilute solution of the purest cupric sulphate acidified with nitric and sulphuric acids, about half the metal was deposited upon the interior of a large platinum dish. The remaining liquid being decanted, the film was washed, re-dissolved, and partially re-deposited through the agency of two Bunsen cells. It was hoped that this fractionation would rid the copper of that probable impurity which almost invariably manifests itself as minute dark spots upon the surface of the film of a completed electrolysis, but the hope proved to be a vain one, and no method of purification was devised which would wholly remove the difficulty. Some of the copper films obtained in the course of the work were almost free from the minute spots, while others of the same series showed a larger number of them; but the phenomenon did not appear to affect the results. From this it would seem that the supposed impurity might have consisted merely of finely divided copper, but even on the worst supposition the amount was so infinitesimal that it could have had no influence upon the observed atomic weight.

The brilliant metallic film thus prepared was carefully separated from the platinum and thoroughly washed with hot water. The separation of the copper from the dish is greatly facilitated by previously rubbing the surface of this electrode with an exceedingly small quantity of pure semi-liquid paraffin, which seems to fill the microscopic cavities of the platinum without interfering with the continuity of the copper film. The pure washed copper was returned to the clean dish, dissolved in very pure nitric acid, and the product slowly converted into basic nitrate, and finally into oxide, by gradually increasing heat. The last part of the operation was conducted at a low red heat in porcelain, and of the product only the central portions were used in the work. The resulting cupric oxide was a fine black powder, which dissolved completely in acids, and gave every evidence of being chemically pure.

A large quantity of this copper oxide was dissolved in a slight excess of pure hydrobromic acid, and the solution evaporated to dryness over a steam bath. Of course, every possible precaution against dust and other impurity was taken with regard to this as well as to every other operation of the research, neither hydrochloric acid nor ammonia being used in the room devoted to it. During the process of evaporation a very faint odour of bromine was perceptible; and upon the subsequent solution of the brilliant black scales of cupric bromide in water, the clear blue liquid slowly deposited a few microscopic crystals of the basic bromide, which will be described in another place. After standing a few days the crystals ceased to be deposited, and the filtered clear odourless solution remained for about four weeks without further change,

serving as the basis of a number of experiments, and furnishing material for the first series of preliminary analysis.

Since it was evidently impossible to obtain the normal salt by the evaporation of the solution at 200° in the air, many attempts were made to prepare it by concentration of the neutral solution over sulphuric acid in air and in nitrogen gas of low tension. The first trials all ended in failure, and it was not until much later that the problem was successfully solved. The purest salt obtained at this stage of the work consisted of brilliant black crystalline scales, which, contrary to all expectation and all literature* upon the subject, were not very deliquescent unless moistened with strong hydrobromic acid. Since the normal compound invariably seems to lose a trace of bromine on exposure to the air, the lack of deliquescence may be due to a very thin superficial covering of the basic bromide. The normal salt is soluble in a very small amount of water, forming a brownish black solution; this becomes deep purple after the addition of hydrobromic acid, and upon gradual dilution goes through successive shades of brown and dirty green to a most beautiful "robin's egg" blue.

The basic salt above alluded to was found to be quite insoluble in water, hence it seemed probable that the dilute solution of cupric bromide from which it had separated was perfectly normal, and it became an important problem to settle this point. As the normal salts of copper are wholly without action upon a solution of methyl orange, this indicator formed the most convenient test for the neutrality of the liquid in question. To about 50 cubic centimetres of the clear solution of pure cupric bromide, which had remained standing for three weeks, were added two drops of a dilute solution (1:400) of methyl orange, and the greenish liquid was thoroughly shaken. Upon equally dividing the solution between two test-tubes, the most careful observation showed no difference in the colour of the separate portions. To one tube was then added 0.05 c.c. of a twentieth normal solution of hydrobromic acid (= 0.2 m.grm. of bromine) and a change from green to grey was perfectly evident when the portions were again compared. A second equal addition of acid produced a purplish hue. The grey was, of course, due to the simultaneous presence of the red colour of the acidified methyl orange, the yellow of the unchanged compound, and the blue of the copper bromide, and proved that some of the indicator had been acted upon by the acid: hence the solution could not have been basic in the first place. In a few words, the solution, containing about one and a half grms. of cupric bromide, could not possibly have lacked more than 0.0002 gm. of its normal weight of bromine. This being the case, a determination of the relative weights of copper and bromine in such a solution would form a sufficiently accurate basis for the calculation of the atomic weight of copper.

Method of Analysis.

The bromine and copper were determined in separate weighed portions of the solution, according to usual methods. For the estimation of the former, the diluted cupric bromide was slowly added to a slight excess of pure argentic nitrate dissolved in 150 cubic centimetres of hot water. In some of the determinations nitric acid was added to the silver nitrate before the precipitation, and in the other cases the acid was added afterward; but the difference in procedure produced no difference in result. The silver bromide settled readily, and was treated in the manner already described (see *ante*).

The copper was determined in another weighed portion of the solution by electrolysis, after the complete expulsion of the bromine by means of nitric and sulphuric acids. One and a half to three grms. of cupric bromide were used in each determination, and usually one part of nitric acid

and two parts of sulphuric acid were taken to decompose one part by weight of the salt; but here again the relative quantities were varied without any perceptible effect upon the result. When the bromine and nitric acid had been expelled over the water bath, the residual copper sulphate and sulphuric acid were dissolved in a small quantity of water, and the whole transferred to the platinum crucible which was to serve as the negative electrode. It was found that within reasonable limits the size of the crucible and the dilution of its contents had no important effect upon the deposition of the copper, provided that the strength of the current was properly regulated. With six gravity cells and eighty ohms external resistance it was possible to deposit perfectly half a gm. of copper in a coherent film from 25 cubic centimetres of solution. The positive electrode consisted in every case of a strong platinum wire fused into the centre of the watch-glass serving as a cover to the crucible. Twice before the completion of each electrolysis the liquid adhering to the lower surface of this lid was washed into the crucible, and the current was always maintained for at least thirty-six hours. Upon breaking the circuit, the sulphuric acid was at once wholly displaced by a stream of distilled water, and after washing by decantation with pure water, alcohol, and ether, the film was finally dried at 95° C. to perfectly constant weight. All the washings were collected in a large porcelain dish, carefully examined in order to be sure that no copper had been carried away, and after evaporation to small bulk tested with uniformly negative result for the presence of traces of metal in solution. It is almost needless to state, that, in every operation involving the quantitative transference of liquid, the original containing vessel was washed out with the most scrupulous care, and finally tested to prove the absence of any trace of its former contents.

Below is the series of four results obtained from the first cupric bromide solution. About two weeks elapsed between the first and last determinations of this series.

PRELIMINARY RESULTS: FIRST SERIES.

Determination of Copper.

No. of experiment.	CuBr ₂ solution taken. Grms.	Copper found (reduced to vacuum). Grms.	Copper in 25 grms. solution (to vac.). Grms.
1	26.400	0.4397	0.4164
2	26.423	0.4401	0.4164
3	52.824	0.8799	0.4164
4	26.454	0.44075	0.4165

Average 0.41642

Determination of Bromine.

No. of experiment.	CuBr ₂ solution taken. Grms.	AgBr found (reduced to vacuum). Grms.	Bromine in 25 grms. solution (to vac.). Grms.
5	26.419	2.5995	1.0468
6	26.436	2.6018	1.0471
7	26.413	2.5996	1.0471
8	26.414	2.5990	1.0468

Average 1.04695

Atomic Weight of Copper.

From above results, if Ag : Br = 108.00 : 80.007, Cu = 63.644.

From results of previous paper, if Ag : Br = 108.00 : 80.007, Cu = 63.640.

According to Hampe, on same basis, Cu = 63.37±

Since atomic weights are in any case relative, the ratio* Ag : Br = 108.00 : 80.007 will be assumed as the present standard of reference, for the sake of convenience and comparison with previous work. Later, all values will be translated into the various generally accepted standards.

* Berthelot, *Ann. de Chim. et de Physique*, 2nd Series, xlv, 386 (1890); Löwig, *Liebig's Handwörterb. Ch.*, iv, 713; Rammelsberg, *Pogg. Ann.*, lv, 246; and many others.

* Although this ratio is not materially different from 108:80, we select it as the mean value of all the most accurate determinations.

The second series of analyses was made from the more dilute solution of a new sample of the salt, prepared in the same manner as the first, but perhaps somewhat less pure. The object was to seek further evidence of the constancy of the composition of dissolved cupric bromide, and it will be seen that the result agrees moderately well with the former one.

PRELIMINARY RESULTS: SECOND SERIES.

Determination of Copper.

No. of experiment.	CuBr ₂ solution taken. Grms.	Copper found (reduced to vacuum). Grms.	Copper in 25 grms. solution (to vac.). Grms.
9	77.875	0.8158	0.26190
10	51.891	0.5435	0.26185

Average.. .. 0.26187

Determination of Bromine.

No. of experiment.	CuBr ₂ solution taken. Grms.	Silver bromide found (reduced to vacuum). Grms.	Bromine in 25 grms. solution (to vac.). Grms.
11	51.871	3.2114	0.65866
12	51.870	3.2113	0.65865
12	40.308	2.4957	0.65871

Average.. .. 0.65867

Atomic weight of copper 63.618

It is certain that the hydrobromic acid used in making this preparation, notwithstanding the care taken in its manufacture, contained a trace of alkali from the glass retort used in distilling; and the presence of this impurity would tend to lower the observed atomic weight of copper. In order to correct this evil, and also in the hope that free hydrobromic acid might prevent the very slight formation of basic salt which invariably took place on the evaporation of water from the neutral salt, the attempt was made to crystallise the cupric bromide from acid solutions. The crystals were still basic, owing to the surface decomposition of exposed scales, but nevertheless two small distinct preparations of such crystals were dissolved, allowed to deposit their basic salt, and each analysed for copper and bromine. Neither of these analyses were wholly satisfactory, but for the sake of completeness their final results are given below.

PRELIMINARY RESULTS: THIRD SERIES.

Solution of Crystals.

No. of experiment.	Weight of copper (reduced to vacuum). Grms.	Weight of AgBr (reduced to vacuum). Grms.	Atomic weight copper. AgBr=188.007
14 and 15	0.2500	1.4771	63.64
16 and 17	0.5473	3.2348	63.62

All the results thus far given were regarded merely as preliminary ones; and a complete series in which all possible care should be taken, both in preparation and analysis, remained still to be made. But before proceeding to the final determinations it was thought well to make several experiments with the object of proving the exactness of certain operations of the work. In the first place, two samples of the asbestos used for filtering were tested several times for constancy in weight, after heating to different temperatures; and the greatest loss of any one mat between 130° C. and 700° C. was found to be less than one tenth of a m.grm.

In the next place the copper films of experiments 1 and 2 were heated in their crucibles to 500° C. in a stream of pure hydrogen, which was supplied through a curved tube and a perforated lid after the manner of Rose. The platinum rim left unprotected by the copper film was so small that absorption of hydrogen must have taken place only in unweighable quantities. No change in the weight of the copper was observed.

Finally, 0.3530 grm. of purest electrolytic copper lost 0.00005 grm. on heating to incipient redness in an atmosphere of hydrogen. After dissolving in nitric and sulphuric acids and electrolysis precisely as usual, the recovered copper weighed 0.35305 grm., indicating a gain of only one-tenth of a m.grm. over the lowest weight previously observed. This gain is not greater than a possible error in weighing; hence, as proof of the accuracy of the electrolytic method and the purity of the materials, the experiment leaves little to be desired.

(To be continued).

NOTICES OF BOOKS.

The Patentee's Guide: Information for all Sorts and Conditions of Inventors in all parts of the World. By H. F. BOUGHTON, M.I.Mech.E., Registered Patent Agent. London: Simpkin, Marshall, and Co., Limited.

THIS work, in addition to the usual information on patent law and patent practice in Britain and in most civilised countries, presents us with the author's views on a variety of subjects not necessarily included in a patentee's guide. Some of these opinions are at least open to criticism. Thus in the initial address the author commits himself to the assertion that the British patent law "is as near perfection as the wit of man can well devise." We must beg to remind him of its two gigantic faults: that it does not, as did the so-called "Old Law," cover all Her Majesty's dominions; and, secondly, that it allows an alien domiciled abroad to obtain and uphold a British patent, refusing all the time to work it upon British soil, though carrying it out at the same time in some foreign country. Thus our patent law is made the means of keeping inventions out of the country and depriving British capital and labour of their legitimate field. An Imperial patent law could be secured, as far as India and the "Crown Colonies" are concerned, by a mere stroke of the pen, giving of course the Calcutta patent office equal scope with that in London. Those Colonies which have obtained *quasi*-independent legislatures would, we think, not hesitate to come on similarly reciprocal conditions. If a Canadian inventor without any additional outlay could obtain at Toronto a patent covering the whole of the British empire he would be immensely the gainer; so would the Australian inventor if he could procure his Imperial patent at Sydney or Melbourne.

In one part of his book the author tells us that "Invention has proved to be the very noblest of sciences or arts, whichever term you wish," and on an earlier page a very similar utterance is ascribed to Mr. Justice Keble. We are unable to imagine the process of mental confusion which can lead any man to call invention a "science."

Nor can it be contended that invention has "found work and pleasure for all." It sometimes, as in the case of artificial alizarine, reduces a prosperous district to destitution. If we grant—a very strong concession—that the "high explosives" may discourage war by rendering it too dreadful, they certainly put additional power into the hands of individual criminals and of conspirators. Another unpleasant fact is that the most lucrative inventions are often those of the least benefit to mankind. A new toy, a new piece of folly may bring in to its author hundreds of thousands, whilst a device proved capable of saving the harvest in a wet season is neglected. No law can prescribe to a man what he may invent or try to invent, but invention nevertheless has its ethics, sadly as they are neglected.

The author recommends that all secret nostrums should be compelled to be patented, their composition being of course made known. We can suggest a more excellent way, which would save Britain from being

the happy hunting ground of a legion of quacks, both native and alien. We would say let all protection in the form of patents, trade-marks, copyright of labels, and advertisements be refused for all proprietary medicines and foods, or for methods of producing them.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Analytische Chemie.
Vol. xxix., Part 3.

A Contribution to the Valuation of Zinc Powder.—G. Klemp.—(See p. 12).

The Volumetric Determination of Zinc according to E. Donath and G. Hattensaur.—L. Blum.—The above-named chemists have recently published (*Chemiker Zeitung*) a method for the titration of zinc with solution of potassium ferrocyanide in a solution of ammonium tartrate. The present author finds that the results of this method are too high if manganese is present.

The Determination of Iodine in its Compounds.—W. Statenbeker.—This paper requires the accompanying cut.

A New Apparatus for Exsiccating Substances of all Kinds under Reduced Atmospheric Pressure.—D. Sidersky.—This paper also requires the accompanying illustration.

Contributions to the Examination of Spirituous Liquors.—W. Fresenius.—This very extensive memoir does not admit of insertion.

A New Method for Determining the Specific Gravity of Gases.—F. G. C. Müller.—The manometer tube used is 600 m.m. wide, slightly curved below, and fixed horizontally. As a manometric liquid the author employs coloured ether. The atmospheric pressure acts upon one end of the liquid column, and at the other the pressure of the column of gas or steam to be measured, which is placed in a vertical glass tube 2 c.m. in width and 120 c.m. in length, open above and filled from below. If this tube is filled with air the liquid in the manometer stands at zero. For gases which are lighter than air the pressure tube is inverted.—(*Zeit. f. Physik. u. chem. Unterricht*).

The Behaviour of Silicates in a Bead of Phosphatic Salt.—K. Haushofer (*Academia zu München*) and J. Hirschwald (*Journ. f. Prakt. Chemie*).—The former author studies the difference in the effects of "microcosmic salt" upon silicates. Hirschwald gives lists of minerals which, when pulverised, dissolve in the microcosmic salt slowly, easily, or very easily.

Sealing up Very Volatile Liquids in Glass Tubes.—W. H. Greene (Franklin Institute).—The author plunges the tube up a line close below the point to be melted into a mixture of salt and snow. For more volatile liquids he uses liquid carbonic acid, or a mixture of nitrous oxide and ether.

A New Spectrophotometer.—G. Hüfner (*Zeit. Physik. Chemie*).—The arrangement is not described.

A Constant Water-Bath.—B. F. Davenport.—From the *Journal of Anal. Chemistry*.—S. J. Speak (CHEMICAL NEWS) mentions that a water-bath on the same principle was used by G. W. Slater eight years ago.

A Water-Bath Regulator.—T. H. Easterfield.—From the CHEMICAL NEWS.

A Trough for Hofmann's Apparatus for Determining Vapour Densities.—T. H. Easterfield.—From the CHEMICAL NEWS.

An Electric Blast.—G. Barthel (*Helfenberger Annalen und Chemiker Zeitung*).—A current produced by means of four Meidinger batteries is carried round an electromagnet and is continually broken and closed by an arrangement on the principle of Wagner's hammer. The vibrations of the keeper thus produced serve to work small bellows constructed of two plates over which is stretched a membrane of caoutchouc. The current of air thus produced is sufficient for a blast-lamp.

A Sampling-Tool.—Kroupa (*Osterr. Zeit. Berg. und Hütten Wesen*).—The instrument is for obtaining average samples from heaps of finely granular materials. Kroupa inserts a spiral turned by a handle in a cylinder upon which a wider vessel is placed. The spiral is made to revolve whilst the cylinder is forced down into the heap.

On Indicators.—From the *Pharm. Journal and Transactions*.

Vanadium in Caustic Alkali.—Baumgarten, Donath, W. Fresenius, and E. F. Smith (Franklin Institute).—On saturating the lye obtained from common stick-potassa with sulphuretted hydrogen, acidulating with hydrochloric acid, and heating for some hours, there was obtained a chocolate-coloured precipitate. This precipitate was dried, extracted with carbon disulphide, dissolved in yellow ammonium sulphide, re-precipitated with hydrochloric acid, again treated with carbon disulphide, and heated. In this manner was obtained from 1.5 kilo. of ordinary potassium hydrate a crystalline residue of 0.5 gm. in weight, which gave the characteristic reactions of vanadium.

Recovery of Uranium Residues.—Laube (*Zeit. Angewandte Chemie*).—See p. 11.

Production of Pure Hydrochloric Acid for Analytical Purposes.—R. Hamilton.—From the CHEMICAL NEWS.

Preparation of Oxygen from Soda Lye, Bromine, and Copper Sulphate.—G. Denigès.—From the *Journ. de Pharm. et de Chimie*.

Purification of Mercury.—P. Schrödter and A. W. Schrödter.—Instead of bamboo the authors use a piece of Spanish cane 12 c.m. in length, secured to the bottom of the funnel by means of a ring of caoutchouc. Over the upper end of the cane is placed a thin layer of wadding cleansed and freed from grease.

Experiments in Oxidation by Means of the Galvanic Current.—Edgar F. Smith.—From the *Journal of the Franklin Institute*.

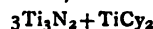
Determination of Lithium.—A. Carnot (*Bulletin de la Soc. Chimique de Paris*).

Determination of Chromium by Means of Hydrogen Peroxide.—A. Carnot (*Bulletin de la Soc. Chimique de Paris*).

The Use of Hydrogen Peroxide in the Determination of Chromium, Manganese, and Iron.—A. Carnot.—From the *Bulletin de la Soc. Chimique de Paris*.

Determination of Chrome and Copper in Iron and Steel with the Use of Sodium Hypophosphite as a Reducing Agent.—C. Reinhardt (*Stahl und Eisen*).—This paper will be inserted by opportunity.

Detection of Titanium and Cyanogen.—C. Lüdeking (*St. Louis Acad. of Science*).—The compound—



(which is often found in iron furnaces on smelting titaniferous ores) may be formed in the inner flame of a Bunsen burner, which is made slightly luminous by a proper regulation of the supply of air. On account of the characteristic appearance of this compound very small quantities of titanic acid can be quickly detected. The substance in question is dissolved in a little sodium carbonate in the loop of a thin platinum cone, and all the sodium is volatilised in the inner flame. If titanium is present, the above-named coppery red compound is

formed, and may be easily recognised on the platinum wire. Inversely the reaction serves for the detection of cyanogen in flames.

Determination of Zinc in Iron Ores.—Rose Finkener. —Five grms. of the ore are dissolved in strong hydrochloric acid. From 2 to 3 c.c. of strong nitric acid are added to the solution, which is evaporated to dryness and filtered. Into the filtrate, which is heated to 80°–100° and strongly acidified, sulphuretted hydrogen is introduced in order to eliminate any copper, arsenic, or antimony which may be present, to convert ferric into ferrous chloride, and to saturate the solution (200 c.c. at least) with sulphuretted hydrogen. If copper is to be determined, and if a precipitate has appeared, it is filtered off along with the liberated sulphur. In the contrary case the filtration is omitted, acetic acid and ammonium acetate are added, and ammonia is added from a burette the delivery tube of which is immersed in the liquid. It is run in at first in large quantities and then drop by drop, keeping the vessel in motion until the precipitate, consisting of zinc sulphide and a little iron sulphide, has taken a grey colour. If the grey colour no longer disappears after the glass has been briskly shaken dilute hydrochloric acid (1:50) is dropped in until it turns white, and dilute ammonia is then again cautiously added until a permanent light grey colour is obtained. On the completion of the precipitation the zinc sulphide coagulates and begins to subside. It is then filtered and washed with water containing acetic acid and sulphuretted hydrogen. The filtrate should be tested as follows:—The filter with its contents is placed in a beaker, a sufficient quantity of dilute hydrochloric acid (1:6) is added, the mixture is stirred, filtered, and washed, if copper sulphide is present, with water containing hydrochloric acid and sulphuretted hydrogen. If cobalt or nickel is present the sulphides of these metals remain undissolved. The sulphuretted hydrogen is expelled from the filtrate by heat, the liquid is let cool, mixed with a slight excess of sodium carbonate, heated to a boil, filtered, and the precipitate of basic zinc carbonate so obtained is dried and ignited. If the precipitate of copper sulphide obtained in the acid solution by means of sulphuretted hydrogen is filtered off, and if the zinc sulphide thus obtained is free from cobalt and nickel sulphides (which is generally the case), it is ignited with powdered sulphur in a current of hydrogen and weighed as zinc sulphide.

A Sensitive Reaction for Copper.—M. Denigès.—From the *Comptes Rendus*.

Separation and Determination of Antimony and Tin.—Lorion.—From the *Journal de Pharmacie et de Chimie*.

Separation and Determination of Chlorine, Bromine, Iodine, and Cyanogen.—G. Crieva.—From the *Gazzetta Chimica* and the *Journal of the Chemical Society*.

Determination of Nitric Acid with Ferrous Sulphate.—Pelouze, modified by Bailhache.—From the *Comptes Rendus*.

Reagent for Aldehyd.—L. Crismer (*Chemiker Zeitung*). —The author recommends a solution obtained by mixing a solution of potassium iodide with mercuric chloride and adding potassa or soda-lye or baryta water. Or Nessler's reagent may be used. In this manner aldehyd may be detected in the watery solution of ethers, in chloroform, in ethereal oils, in glycerin, &c.

Fermentability of Galactose.—Em. Bourquelot.—From the *Comptes Rendus*.

MISCELLANEOUS.

Sulphate of Copper.—We have been requested by the Vice-Consul of a foreign government to supply them with statistics relative to the production and consumption of sulphate of copper in the United Kingdom. We shall

esteem it a favour if any of our correspondents will indicate how best to procure what is required.

The Douglas Oil Gas Lamp.—We understand that Messrs. J. Griffin and Sons, of Garrick Street, Covent Garden, have now received some of these lamps, which were described in the *CHEMICAL NEWS*, vol. lxii., p. 84. They have tried them, and find them very satisfactory. They will be glad to show them in operation to any one interested.

Announcement.—Mr. W. H. Stanger and Mr. Bertram Bount, of the Broadway Laboratory and Testing Works, Westminster, desire to correct a rumour which has become prevalent, by stating that the Mr. William Fox who is at present associated with them at the above address is a Member of the Institution of Civil Engineers and not a practising analyst.

Messrs. May and Baker.—We are informed by a circular signed by Messrs. W. G. Baker, R. C. Heath, and W. E. B. Blenkinsop, that the business of this firm will in future be carried on by a limited company at Garden Wharf, Battersea. The conversion of the firm into a company will involve no change in the mode of conducting the business. Mr. Blenkinsop, to whom the manufacturing department has for several years been entrusted, will be the managing director.

Popular Lectures on Chemistry.—In response to a widely expressed demand from the students who attended the former lectures on chemistry, the Battersea Polytechnic Committee have arranged for a course of ten popular lectures (with experiments) by Professor V. B. Lewes, on the Chemistry of Arts and Manufactures, at Crichton Hall, Clapham Junction. The lectures will be delivered on Tuesdays, commencing January 13th, at 8 p.m., and will include the following subjects:—Colour-paint, Iron, Copper, Lead, Zinc, Tin; the Alloys; the Acids; Soap, Soda, and Glass. Tickets for the course of ten lectures (4s.) may be obtained from the Hon. Secs., Messrs. H. Genochio and J. Harwood, on the evenings of the lectures at Crichton Hall.

MEETINGS FOR THE WEEK.

MONDAY, 12th.—Medical, 8.30.
TUESDAY, 13th.—Royal Medical and Chirurgical, 8.30.
—Photographic, 8.
—Institute of Civil Engineers, 8.
WEDNESDAY, 14th.—Society of Arts, 8. "Steam Lifeboats," by J. F. Green.
THURSDAY, 15th.—Royal, 4.30.
—Institute of Electrical Engineers, 8.
FRIDAY, 16th.—Quekett, 8.
—Physical, 5. "Photo-electricity," by Prof. G. W. Minchin, M.A. "A Lecture-room Method of Determining 'g,'" by Prof. Barrell, B.A. "On the Change in the Absorption Spectrum of Cobalt Glass Produced by Heat," by Sir John Conroy, M.A., Bart.

TO CORRESPONDENTS.

F. J. Chalmers.—We do not know of any book treating on the metallurgy and mining of tin ores. A very complete account is to be found in the first volume of "Ker's Treatise on Metallurgy," by W. Crookes, published by Longmans and Co.

BAILLIERE, TINDALL, & COX'S NEW BOOKS.

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Aids to Sanitary Science, for the Use of CANDIDATES for PUBLIC HEALTH QUALIFICATIONS. By F. J. ALLAN, M.D., Dip. Pub. Health, Camb., Assistant Prof. of Hygiene, Coll. of State Med., 236 pp., price 4s. 6d., cloth.
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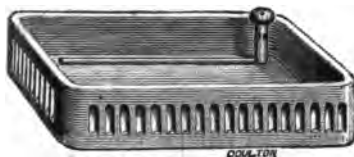
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January 9, 1891.

THE CHEMICAL NEWS.

VOL. LXIII. No. 1625.

ON WOLF AND RAYET'S BRIGHT-LINE STARS IN CYGNUS.*

By WILLIAM HUGGINS, D.C.L., LL.D., F.R.S.,
and Mrs. HUGGINS.

In 1867 M.M. Wolf and Rayet discovered at the Paris Observatory three small stars in Cygnus, which in the spectroscope showed several bright lines upon a continuous spectrum.† All three stars have a very bright band in the blue part of the spectrum.

These stars are:—

B.D. + 35°, No. 4001.

B.D. + 35°, No. 4013.

B.D. + 36°, No. 3956.

Their spectra were described in 1873 by Vogel, whose observations agree substantially with the original description given by Wolf and Rayet.‡ A more complete

not an identical position in all three stars, nevertheless support substantially his earlier observations, which Vogel considered to show, contrary to the statements of Secchi, that the bright lines, including the blue band, were not due to carbon.

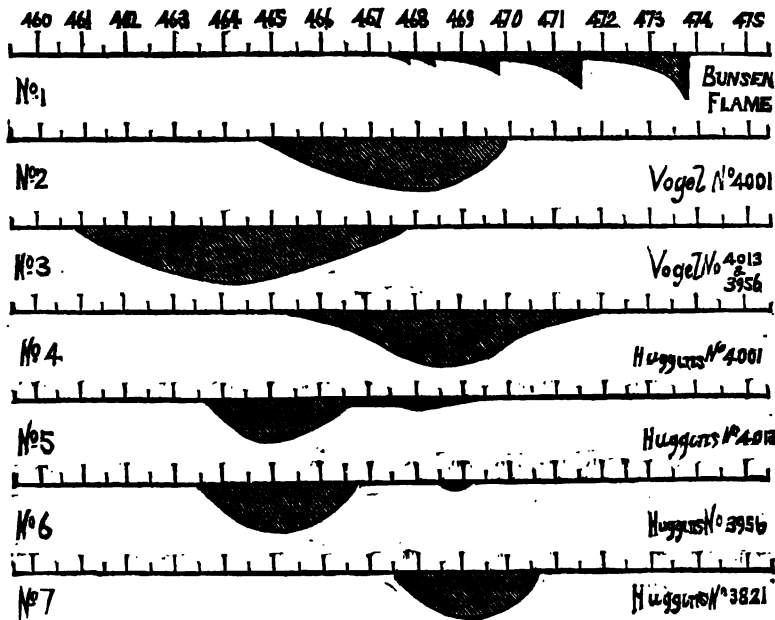
In the diagram, Nos. 1, 2, and 3 show the positions of the bright bands in the three stars, according to Vogel's measures, relatively to the blue band of the hydrocarbon flame.

Vogel's measures are:—

Star No.	Beginning of the band.	Brightest part.	End of the band.
4001	λ 470	λ 468	λ 465
" 4013	—	λ 464	—
" 3956	λ 468	λ 464	λ 461

His diagram shows the band in No. 4013 to begin and end at about the same positions as in the star 3956.

It has been stated recently that the bright blue band in all three stars is the carbon band in the blue, commencing near λ 474* ; and more recently, notwithstanding the difference of position, according to Vogel, of the band in one of the stars from that which it occupies in the other two of as much as λ 0040, that direct comparisons showed an absolute coincidence of the band in all three stars with the blue band of a spirit-lamp flame.†



account of their spectra was given by Vogel in 1883, from observations at Vienna with the 27 inch refractor made by Sir Howard Grubb.‡

Vogel's measures of the bright blue band place it in the star No. 3956 at from λ 468 to λ 461, with a maximum at λ 464; in the star No. 4013, with a maximum at the same place in the spectrum; while the corresponding blue band in the star No. 4001 has a considerably less refrangible position, commencing at λ 470, reaching a maximum at λ 468, and ending about λ 465.

These latter measures, though they differ from his earlier ones, in so far as they show that the blue band has

* From the Authors. A Paper read before the Royal Society, Dec., 1890.

† *Comptes Rendus*, vol. lxx., 1867, p. 292.

‡ *Berichte K. Sächs. Ges. der Wiss.*, Dec., 1873, p. 556.

§ *Publication Astrophys. Observ. Potsdam*, vol. iv., No. 14, pp. 17 to 21.

* Professor Lockyer, in the Bakerian Lecture for 1888 (*Roy. Soc. Proc.*, vol. xli., p. 37), says of the star No. 4001:—"The bright band with its maximum at λ 468 is the bright carbon fluting commencing at λ 474 and extending towards the blue, with its maximum at 468, as photographed at Kensington."

Of the star 4013:—"The bright band in the blue at 473 is most probably the carbon band bright upon a faint continuous spectrum, this producing the absorption from 466 to 473" (*loc. cit.*, p. 41).

Of the star No. 3956:—"The bright band at 470 is the carbon band in the blue, commencing at 474, with its maximum at about 468, as observed and photographed at Kensington" (*loc. cit.*, p. 43). See Vogel's measures for the band in this star, which are given in the text.

Diagrams of the spectra of these stars are given at pp. 38, 40, and 41, based on Vogel's observations and his curves, which, on a slightly reduced scale, are placed at the bottom of the diagrams. The maximum of Vogel's curves is placed in all three diagrams at λ 468, and agrees in the diagrams with the carbon band; whereas Vogel's original curves and his measures place the maximum in the case of two of the stars at λ 464, beyond the carbon band.

† Professor Lockyer, in a signed article in *Nature* (August 7, 1890, vol. xlii., p. 344), writes:—

"In the Bakerian Lecture for 1888 I gave a complete discussion of

As the presence or absence of carbon in these stars, as shown by the coincidence or otherwise of the blue band with that of the hydrocarbon flame, was of great importance to us in connection with a wider investigation on which we are at work, we thought it necessary, after these recent statements as to the position of the band, to make direct comparisons of the spectra of these stars with that of the hydrocarbon flame under sufficiently large dispersion to enable us to determine whether Vogel's measures are substantially correct, or whether they are so largely in error as the absolute coincidence of the band with the blue band of a spirit-lamp flame in the case of all three stars would show them to be.

The obvious importance of making the observations with sufficient dispersion is supported by Vogel's own experience. With the small dispersion which he employed in his earlier observations in 1873, he did not detect the large difference of position, about λ 0040, of the band in No. 4001, as compared with its position in the other two stars. On this point Vogel says, in his memoir of 1883:—"Etwas abweichend ist nur die Auffassung der Lage der breiten hellen Bande im Blau, die bei den früheren Messungen bei allen drei Sternen übereinstimmt. . . . Bei den verhältnissmässig geringen optischen Hilfsmitteln, mit denen jene Messungen ausgeführt wurden, ist die Uebereinstimmung aber eine ganz überraschende" (*loc. cit.*, p. 21).

We observed the spectra of the stars successively, first with a direct vision prism of small dispersion, then with a spectroscopic (A) containing one prism of 60° , and finally with a spectroscopic (B) with two compound prisms, equal to about four prisms of 60° ; with the last-named instrument the comparisons with the hydrocarbon flame were made.

A rapid preliminary comparison in the spectroscopic (B) of the spectra of the three stars with the blue base of a Bunsen flame showed at once the substantial accuracy of Vogel's measures, and the striking difference of position of the band in the star No. 4001 from that which it holds in the other two stars.

The obvious want of agreement of the star bands with the blue band of the Bunsen flame was seen at once. Their relative positions appeared to agree substantially with the positions represented in No. 2 and No. 3 of the diagram, which are based on Vogel's measures. More careful and repeated observations brought out clearly, as is indeed shown by Vogel's curve, that the star bands differ in character as well as in position from the blue band of the hydrocarbon flame, and also in some respects from each other.

Before giving in more detail the results of our observation on each of the three stars, it should be stated that in all the stars the continuous spectrum is not in our instruments a short one, ending before the position of the bright blue band is reached. On the contrary, an examination with all three spectroscopes showed that the continuous spectrum, though enfeebled by absorption a little before reaching the blue band, can be traced, as is shown in Vogel's curves, quite up to the band, and, indeed, extends for a long distance into the violet beyond the blue band. The blue band does not in our instruments stand out bright beyond the end of a short continuous spectrum, but falls upon a fairly luminous continuous spectrum, which can be traced past the blue band into the violet, apparently as far as the eye could be expected to follow it.

the spectra of bright-lined stars, as far as the observations went, and the conclusion arrived at was that they were nothing more than swarms of meteorites a little more condensed than those which we know as nebulae. The main argument in favour of this conclusion was the presence of the bright fluting of carbon which extends from 468 to 474. This standing out bright beyond their short continuous spectrum gives rise to an apparent absorption band in the blue. . . . Direct comparisons of the spectrum of all the three stars in Cygnus with the flame of a spirit-lamp have been made by Mr. Fowler, and these showed an absolute coincidence of the bright band in the stars with the blue band of carbon seen in the flame. It was found quite easy to get the narrow spectrum of the star superposed upon the broader spectrum of the flame so that both could be observed simultaneously.*

We suspected bright lines or bands in the region more refrangible than the blue band, but in such faint objects this is a point which should be determined by photography.

Professor E. C. Pickering has since kindly informed us that his photographs of the star No. 4001, which extend into the ultra-violet region, show beyond the blue band the bright hydrogen lines at 434, 470, 397, and 389; and also other bright lines at 462, 455, 420, 406, 402, 395, and 388.

In his photographs of the stars 4013 and 3956, however, the only well-marked line is in the blue at 470.

Star 4001.—In this star, as is shown by Vogel's measures and curve, the bright blue band is less refrangible than in the other two stars, and approaches therefore nearer to the position of the blue band of the hydrocarbon flame. The appearance and position of the band in the star as contrasted with that of carbon, when observed in spectroscopic B, are represented in spectrum No. 4 of the diagram.

The brightest part of the band, from about λ 468 to λ 469, falls off rather suddenly in brightness at about these wave-lengths, but can be traced towards the red as far as about λ 471.5, and as far in the blue as about λ 465.5.

In our observations of this and the other stars we did not attempt micrometric measures of the blue band, but we estimated their positions by means of the intervals between the five flutings of the band of the Bunsen flame. In the case of objects so faint in our instrument when viewed under the dispersion of spectroscopic B, we did not consider there would be any real gain of accuracy by attempting to take measures.

Though the wave lengths assigned to our positions must therefore be regarded as not more than approximately correct, we have no hesitation in considering them fully accurate enough for the purpose of our investigation.

The star band is not split up into well-separated maxima, as is the Bunsen flame band, but we have little doubt that the brightest part of the band, from λ 468 to λ 469, which is much, and rather suddenly, brighter than its beginning and termination, consists of bright lines. Lines appear to flash out at moments, but in our instruments they cannot be seen with sufficient steadiness for us to be sure of their number and position.

Under certain conditions of the electric discharge, the normal relative brightness of the component flutings of the blue hydrocarbon band has been observed to be so far changed that the position of maximum intensity is moved from the less refrangible end of the band towards the blue end; but the five flutings remain without any change of their position in the spectrum.*

Dr. Hasselberg, by means of feeble disruptive discharges from tin-foil terminals placed outside an exhausted tube containing vapour of benzole, obtained a nearly pure spectrum of the order of that in a hydrocarbon flame mixed only with faint lines of hydrogen. He says:—"Es war aber hier die violette Gruppe sehr schwach. Dagegen schien mir die blaue Gruppe relativ heller als im Flammenspektrum, und sie hatte ausserdem entschieden ihre grösste Intensität nicht an der weniger brechbaren Kante, sondern mehr nach dem Violetten hin. Dasselbe schien mir auch mit der gelben Gruppe der Fall zu sein. In Bezug auf die grüne Gruppe konnte ich aber keine Verschiebung des Intensitätsmaximums bemerken."

Dr. Hasselberg gives curves to show the amount of

* It is necessary to state that the maximum luminosity of the blue band, under some conditions, is about 468. . . . The conditions under which this band has its maximum luminosity at 468 in Geissler tubes seem to be those of maximum conductivity. If the pressure be high, all the members of the group are sharp, and the luminosity of the band is almost uniform throughout. This always occurs when the pressure is very low. At intermediate stages of pressure, however, the luminosity has a very decided maximum at about 468. (Appendix to the Bakerian Lecture for 1868, *Proc. Roy. Soc.*, vol. xlv, pp. 167, 168).

this change of intensity in the blue group and in the orange group. In the blue group the maximum is moved from the first to the third line, that is, to about λ 4698. His curve gives the brightness of the maximum over that of the first line as about 7 to 6, whereas the normal relative intensity of these two lines is in the inverse direction and as about 2 to 4 (Watts' "Index of Spectra," p. 30).*

A similar change from the normal relation of brightness of the flutings within the band, even if removed to λ 468, does not seem to us to bring the star band sufficiently into accordance in character and position with those of the band of the hydrocarbon flame to justify us in attributing the blue band in the star to carbon. Though we traced the band a little further towards the red, than the position of the beginning of the band given by Vogel's measures, yet it is very faint, and without any increase in brightness at the place of the second fluting of the carbon band, beyond which we were unable to see it.

According to Hasselberg's curve, the second bright fluting, where in our instruments the star band ends, still retains a brightness of about 11/12 of that of the maximum, and the first line, at the position of which no brightening of the feeble continuous spectrum of the star could be detected, a brightness of about 6/7 of that of the maximum. That the flutings of the band were not obscured by the absorption band at this part of the spectrum appears clear from the circumstance that we could trace the faint continuous spectrum up to the bright band.

Vogel's and our observations agree in making the band run on some distance beyond the visible termination of the blue band of the Bunsen flame. Piazzi Smyth, under some conditions, observed a large number of faint "linelets" beyond the "5th leader" of the band, where its visibility usually ends; and in the brilliant light of the arc the band can be traced further in the blue. The extension of the band under such circumstances does not seem to us to affect our present argument; for in the very feeble light of the star we may surely take it that the carbon band, if present, could not be seen to extend further than its usual visible limit in a Bunsen flame, namely, about λ 468.

Perhaps it should be stated in connection with the circumstance that we saw the band extend a little further towards the red than Vogel did, that at the time of our observations the hydrogen line at F was not visible in our instruments, whereas it was bright at the time when Vogel observed the star. In the spectrum of a similar star, D.M.+37° 3821, in which the hydrogen line at F at the time was bright, the blue band was seen by us to stop near the place given by Vogel in his measures of the star No. 4001.

Not only is there no coincidence, so far as Vogel and we have observed, of the position of the band in the star with that of the blue band of the Bunsen flame; but, further, the want of accordance of its general characters is so great as to make the view that its origin is carbon very improbable. This improbability is very greatly increased when we find, as will be shown presently, that no traces whatever of the very bright beginnings of the more brilliant green and orange bands could be detected by us in any of the stars. Further, Professor E. C. Pickering has kindly sent to us an account of his photographs of this star, which, though they show the hydrogen line at λ 434, do not exhibit any brightness at the positions of the indigo hydrocarbon bands, beginning near λ 4312, and λ 4382.

This star, however, can scarcely be taken by itself; in the case of the other two stars, in the spectra of which, according to Vogel's, Copeland's, and our own observations, the brightest part of the blue band is from λ 464 to λ 465, but nearer λ 465, quite outside the ordinary visible limit of the carbon band, the evidence seems very strong indeed that the band does not owe its origin to carbon.

We satisfied ourselves that when the spectrum of the star is examined under the dispersion of spectroscopic B, none of the brighter parts of its spectrum fell at, or very near, the green, orange, and indigo flutings of the hydrocarbon flame spectrum; at these positions we were unable to detect any sensible brightening of the star's spectrum. Professor Copeland's measure of the blue band in 1884 was λ 469'5.

No. 4013.—Vogel does not give measures of the beginning and the ending of the band in this star, but only of the brightest part:—"Hellste Stelle, nahezu Mitte, einer breiten verwachsenen Bande, λ 464." He gives, however, a diagram of the spectrum in which the bright blue band is represented as substantially coincident in position and in general character with that in the spectrum of No. 3956.

Our observations agree substantially with those of Vogel, but they make the band to consist of two parts, a very bright part, from about λ 466 to λ 464, but brightest near λ 465; and a very faint band, apparently detached from the bright one from about λ 4685 to about λ 4705. This faint band is brightest near where it ends rather abruptly at the more refrangible end. The very bright band has not the character of a fluting, nor is it broken up into maxima widely separated like those of the Bunsen flame band, but appears to be a group of bright lines. The lines were only glimpsed at moments; it is therefore difficult to make a drawing which truly represents the character of the band as seen in our instruments. The band which is shown at No. 5 of the diagram is left unfinished at the more refrangible end, as we were not certain how far we ought to consider it to extend.

In this star (as we shall show to be the case in No. 3956 also) the great body of bright radiation lies far beyond the ordinary visible limit of the blue carbon band, and no connection whatever with carbon is even suggested to us by the star's spectrum. Dr. Copeland's measure of the band in 1884 was λ 465'4.

The continuous spectrum of the star is unequally bright from the presence of bright groups and also apparently of absorption bands or lines, and therefore with small dispersion it might be easily supposed that the spectrum is brighter at the position of the green carbon band. We examined the continuous spectrum repeatedly with great care, and we were able to satisfy ourselves that, under the considerable dispersion of our instruments, there was no sensible brightening of the spectrum at the positions of the green and of the orange bands of the Bunsen flame.

No. 3956.—Vogel places the brightest part of the band in this star at the same position in the spectrum as in the star last considered, No. 4013, namely, at λ 464, a position beyond the carbon band. The position of the band as it appeared in spectroscopic B with the third eye-piece is represented at No. 6 in the diagram. The position of the band relatively to that of the Bunsen flame was determined by estimations made by means of the intervals between the bright flutings of the Bunsen band. The position agrees substantially with that given by Vogel, but places the maximum brightness nearer to 465. This bright part probably consists of a group of bright lines, and falls off rather suddenly at both ends. We were not certain if the light beyond this bright part was due to a continuation of the band or to the continuous spectrum; more or less dimmed by absorption; we have, therefore left the ends of the band incompleting in the diagram. Copeland's measure of this band in 1884 was λ 464'9.

The sub band seen in the star No. 4013 is very much fainter in this star, but we have little doubt that there is a very faint band present at about the same place in the spectrum.

Professor E. C. Pickering has found in the near neighbourhood of these three stars other stars possessing bright lines in their spectra.* The brightest of these, indepen-

* "The following list contains the designations of all eight stars (with bright lines), the first four being those previously known:—

* *Mém. de l'Acad. Imp. des Sciences de St. Pétersbourg*, vol. xxii., No. 2, 1880, p. 82.

dently discovered by Dr. Copeland in 1884,* namely, D.M. + 37° 38'21, in which the spectrum is similar to that of the Wolf-Rayet stars, was examined. Dr. Copeland says of this star:—"It has a spectrum of several bright lines near D, and a very bright band in wave-length 464" (*loc. cit.*). We were therefore surprised to find the blue band, which is very brilliant, not in the position of the band in the stars No. 4013 and No. 3956, but less refrangible, corresponding to the position of the band in the star No. 4001.

The bright line begins about λ 467 and runs on to nearly λ 470.5. It is clearly not made up of flutings similar to those of the Bunsen flame, but is a group of lines nearly uniformly bright throughout the length of the band. The band did not appear to extend in our instruments towards the red quite so far as the band of No. 4001; it stops near the place assigned by Vogel to the beginning of the band of No. 4001.

The band is represented in spectrum No. 7 in the diagram. Direct comparison with hydrogen showed that the line at F is brilliant in this star.

After some scrutiny of this part of the star's spectrum, we became conscious of a very feeble brightening of the spectrum beyond the bright band towards the violet, and as far as we could estimate its position, at about from λ 464 to λ 467, that is to say, about the position assigned to the band by Dr. Copeland in 1884.

We then re-examined the spectrum of No. 4001, and were able to feel pretty sure that a similar faint brightening of the spectrum occurs in this star also at the same place, namely, about the more refrangible position of the blue band in the stars No. 4013 and No. 3956.

(To be continued.)

FURTHER CONTRIBUTIONS TO THE METALLURGY OF BISMUTH.†

By EDWARD MATTHEY, F.S.A., F.C.S., A.R.S.M.

IN October, 1887, I read a paper before the Royal Society‡ upon a new method which I incidentally discovered while working with a view to separate copper from bismuth, by fusion with bismuth sulphide.

I stated in this paper that bismuth "frequently contains a small proportion of copper, an element most detrimental even in small traces, and hitherto only eliminated by a wet process, costly in practice and tedious in operation. It is necessary by such method to dissolve up the whole of the alloy and precipitate the bismuth in the usual manner—a bulky operation, and one requiring a considerable amount of time. It became therefore advisable, in order to treat cupriferous bismuth rapidly and upon a commercial scale, to effect this separation, if possible, by means of a dry process."

In further researches in the metallurgy of this interesting metal, a case was found in which bismuth contained a very small proportion of copper, under 0.5 per cent, but sufficient to render the metal useless, and, in fact, to destroy those characteristic properties upon which its industrial applications depend.

Instead of treating this cupriferous bismuth by fusion with bismuth sulphide, which necessitates a temperature sufficiently elevated to bring about a complete fusion of the bismuth sulphide, and consequently, unless very great care be taken, great loss by volatilisation of bismuth, it occurred to me to fuse the alloy, and at a temperature a little above its melting-point to add a

small proportion of sodium monosulphide. The mass was then stirred well so as to bring every portion of the fused alloy into contact with the fused sulphide.

After about one hour's stirring, a test was made of the molten metal, and it was found that the amount of copper in it was very considerably decreased.

By skimming off the film of scoria which had risen to the surface, adding a further small proportion of the sodium monosulphide, and continuing the operation of stirring, every trace of copper was eliminated and the bismuth so freed from copper rendered in every way suitable for industrial use.

The first experiment was made upon a quantity of 105 kilogrms., which yielded 94 kilogrms. of bismuth free from copper, and about 11 kilogrms. of skimmings containing the whole of the copper, their bismuth contents of course being available for reduction with further and larger quantities of skimmings as they accumulated.

This process has been repeated upon very considerable quantities of cupriferous bismuth, and has proved to be successful.

This question of keeping the temperature low is of much importance, for the lower the temperature the less tendency there is for the bismuth to volatilise, and as it is necessary to obtain the bismuth free from traces of impurity, which entirely change its nature, it will be seen that any improvement in manipulation, or in the process itself, which enables pure metal to be obtained possesses much interest.

ON THE POTASSIUM CYANIDE ASSAY OF LEAD ORES.

By ARTHUR W. WARWICK,
Assayer at the Phoenix Test Works, Battersea.

THERE being considerable doubt as to the exact value of the cyanide assay of lead ores, some writers on assaying speaking favourably and others disparagingly of it, I thought a few comparative experiments might be of interest to assayers. Mitchell, writing on the potassium carbonate assay, rather unfavourably dismisses the cyanide assay with a couple of lines. Ricketts* states that the cyanide assay gives lower results than the black flux assay, but that it gives cleaner buttons. The ores experimented on were (1) a galena with a siliceous gangue, the lead, however, containing but a small amount of other base metals, (2) a rather poorer galena containing a considerable quantity of copper pyrites, (3) a pure specimen of galena. A few experiments were likewise made with a pure sample of cerussite.

Sampling.

A quantity of the ore experimented upon was crushed and passed through a 60 sieve. When a quantity of the sample was required for an assay, the whole was spread out evenly over a space of about six inches square, and lines ruled down and across, making squares of about one inch; from the centre of each square a small quantity was taken on the end of a spatula, and the required quantity weighed from this smaller quantity. By this means perfectly uniform samples were taken.

The galena (1) first experimented on contained 64.8 per cent of lead. The gangue was quartz. 150 grains of this galena were mixed with 450 grains of potassium cyanide ("gold"). A Battersea crucible, size D, was taken, and a quantity of cyanide well rammed into it. The ore and cyanide was placed above this ramming, and covered with a layer of half an inch of cyanide; the whole was then covered with salt. The amount of cyanide used as ramming came to about 150 grains. The charge was heated at a low red for 15 minutes, and slightly raised for a further period of 5 minutes, when it was withdrawn from

* "Notes on Assaying," New York.

35° 4001, 35° 4013, 36° 3956, 36° 3987, 37° 3821, 38° 4010, 37° 3871, 35° 3954 or 3953. Of these 37° 3871 is P Cygni, and 37° 3821 is the star in the spectrum of which the bright lines are most distinct" (letter in *Nature*, vol. xxiv, p. 440.)

* *Monthly Notices, R.A.S.*, vol. xiv., p. 91, 1884.

† Read before the Royal Society, January 6, 1891.

‡ *Proc. Roy. Soc.*, vol. xliii., page 172.

the furnace, allowed to cool, and the button of lead obtained by breaking the crucible.

Experiment.	Grains of ore.	Grains.	Per cent.
1.	150 gave a button of	87	58
2.	150 "	86.6	57.73

The buttons were very clean and so soft that they could be scratched with the finger nail. The slag was of a pinkish white colour, but there was a brownish white core just above the button. No traces of undecomposed galena could be seen.

Pure potassium cyanide being expensive, experiments were made using in its stead the commercial cyanide. The "stick" cyanide supplied by Messrs. Becker's, Hatton Wall, was the cyanide employed. In order to allow for the decreased purity of the flux, the amount used was raised to 600 grains, the amount of the covering, &c., however, remaining the same.

The amount of ore used, the temperature, and the time were the same as in experiments 1 and 2.

Experiment.	Per cent.
3. 150 grs. galena gave	86.3 grs. lead = 57.53
4. 150 "	86.4 " = 57.6

The difference between the experiments being so small there can be no objection to using the commercial cyanide. The following experiments, however, show the necessity of using an increased amount of cyanide. 150 grains of galena were mixed with 450 grains of "stick" cyanide, using 50 grains for the ramming, and 100 grains for the covering, salt to cover as usual; this charge was treated as in experiments 1 and 2.

Experiment.	Per cent.
5. 150 grs. galena gave	76 grs. lead = 50.6
6. 150 "	74.5 " = 49.6

The slags yielded by these six assays were very similar, differing only in the degree of pinkishness. This sample became too small to be able to make any comparable assays, so that the pure sample was worked upon next, "stick" cyanide being used instead of the "gold" quality. The quantity of cyanide used was that recommended by Ricketts, viz., three times that of the ore, making allowance, however, for the difference in quality of the cyanides used. 100 grains of pure galena was mixed with 500 grains of "stick" cyanide, using in addition 50 grains for the ramming, the whole covered with salt. This charge was heated for 15 minutes at a low red heat, and the temperature raised to a fair red heat for 5 minutes.

Experiment.	Grains galena.	Grains.	Per cent.
7.	100 gave a button of	76.0	76
8.	100 "	76.2	76.2

The slag was black and slightly spongy. A quantity of undecomposed galena could be seen floating on the surface of the salt covering on withdrawing the crucible from the furnace, and in order to overcome this the amount of cyanide used to mix with the ore was increased to 600 grains, and a covering of about 80 grains of cyanide used, the whole being covered with salt. The crucible was heated at a low red temperature to commence with, raising the temperature slowly till it was a bright red. The time given was 20 minutes, counting from the time the crucible was red.

Experiment.	Per cent.
9. 100 grs. galena gave	79.1 grs. lead = 79.1
10. 100 "	79.3 " = 79.3

The slag was black and rather earthy in texture.

The above experiments show the reason why Ricketts says that the cyanide assay gives low results, the reason being, no doubt, that the amount of cyanide used was too small.

In order to thoroughly test the method, a few other assays were made upon the pure galena. The black flux substitute assay was first made. 100 grains of galena were mixed with 375 grs. of black flux substitute, made by mixing two parts of carbonate of soda with one each of flour and borax glass. Three nails, heads downward, were placed in a crucible, and the above mixture charged into the crucible. The mixture was covered with borax, and fused at a red heat until the charge was well fused and free from bubbling, kept at this temperature for five minutes, when the nails were withdrawn and the charge poured into a hemispherical mould; the button freed from adhering slag in the usual way and weighed gave a mean result of 0.8 per cent below the mean cyanide assay.

Experiment.	Per cent.
11. 100 grs. galena gave	78.3 grs. lead = 78.3
12. 100 "	78.5 " = 78.5

Ricketts gives 78.5 as the usual result of this assay. Phillips ("Elements of Metallurgy"), gives 75-78 per cent. Another method was tried. Ore, 200 grains, was mixed with sodium carbonate 300, argol 30 grains, and three nails, salt to cover. This charge was placed in a clay crucible, and heated at a red heat until fusion ensued and all bubbling finished; the charge was kept in the furnace five minutes longer, when the nails were withdrawn and the charge poured, giving results about 6.5 per cent lower than the cyanide assay. Phillips remarks that the alkaline flux assay yields about 70 per cent of lead from pure galena. Ricketts finds that by using the bicarbonate of soda that from 73.0-73.4 per cent of lead can be obtained.

Experiment.	Per cent.
13. 200 grains gave	145.3 grains lead = 72.65
14. 200 "	145.6 " = 72.80

The foregoing experiments are quite sufficient to show that with pure galena the cyanide assay is as perfectly reliable as most dry assays. The galena containing the pyrites had a few comparative assays made upon it. The cyanide assay was performed exactly as in experiments 9 and 10, and the black flux assay as in experiments 11 and 12.

Experiment.	Per cent lead.
15. Cyanide assay gave	56
16. " " "	55.7
Mean 55.85.	

Exp.	Per cent lead.
17. Black flux substitute assay gave	54.0
18. " " "	54.6
Mean 54.3.	

These experiments show that with poor and impure lead ores the potassium cyanide assay has an advantage of 1.5 per cent over the black flux substitute assay.

Cerussite was the next sample experimented upon. The sampling was performed as before. The cerussite used was a very pure specimen from the Broken Hill district, but was not very argentiferous. 100 grains of the cerussite were mixed with 600 grains of cyanide and placed in a crucible prepared as in experiments 9 and 10, and fused at a low temperature for 15 minutes, during which time a rather violent bubbling took place, but was fairly tranquil at the end of that time. The temperature was slightly raised for five minutes, the charge withdrawn, and the crucible allowed to cool and broken.

Experiment.	Per cent.
19. 100 grs. cerussite gave	74.6 grs. lead = 74.6

The slag was pinkish white on the top and next to the crucible, but contained a white crystalline core. The button, however, had a rather vesicular appearance, as if all the CO₂ had not been expelled. In the next experiment the temperature was rather higher, and the time (20 minutes) counted from the time the fusion of the charge commenced.

Expt. no.	Per cent.
20. 100 grs. cerussite gave 75 grs. lead = 75.0	

The foregoing experiments show that the potassium cyanide assay when carefully performed is capable of giving with rich ores results as trustworthy as the best of the other methods, and is to be preferred when the ore is poor. The precautions to be observed are that the temperature be not allowed to rise too high, the time not to exceed 20 minutes, and that the amount of cyanide used be not too small. When these precautions are observed the method gives perfectly trustworthy results. The furnace in which the fusions were performed was Fletcher's gas furnace. For convenience in working and control of the temperature it is to be preferred, when moderate temperatures are required, to the coke furnace.

The proprietors of the works, Messrs. Bowes, Scott, and Western, allowing me to continue the experiments to other ores of lead, I hope to be able to publish further results shortly.

ON GASEOUS ILLUMINANTS.*

By Professor VIVIAN B. LEWES.

III.

ORDINARY coal gas of an illuminating power of 14 to 16 candles can be produced at a fairly low rate, but if a higher quality is required considerable additional expense has to be incurred in order to enrich it. Up to now, the material almost universally employed for this purpose had been cannel; but as this article is rapidly rising in price, and the best qualities are not easily obtainable, attention is being seriously directed to other means of bringing up the illuminating power of gas. This question of enrichment has been the study of inventors from the earliest days of the gas industry; and the methods employed for this purpose may be classified as:—(1) The carburetting of low-power gas by impregnating it with the vapour of volatile hydrocarbons. (2) Enriching the gas by vapours and permanent gases obtained by the decomposition of the tar formed at the same time as the gas. (3) Mixing with the coal gas, oil gas obtained by decomposing crude oils by heat. (4) Mixing with the coal gas, water gas which has been highly carburetted by passing it, with the vapours of various hydrocarbons, through superheaters, in order to give permanency to the hydrocarbon gases.

In the first method, many points have to be taken into consideration, as the hydrocarbons which have from time to time been used for this purpose vary so greatly in composition. A very volatile naphtha, although it evaporates quickly and larger quantities of its vapour are taken up by the gas, often giving a less increase of luminosity than a heavier hydrocarbon, of which but little is vapourised.

The great trouble which presented itself in the older carburetting systems was that all the commercial samples of naphtha are mixtures of various hydrocarbons, each having its own boiling-point, and that, therefore, when used in any of the old forms of carburetters, they gave up their more volatile constituents very freely at the beginning of the experiment, while the amount rapidly diminished as the boiling-point of the residue became higher; so that when 2113 cubic feet of poor coal gas were passed through a naphtha having a specific gravity of 0.869 and a boiling-point of 103° C., the temperature during the experiment being 22° C., the first 80 cubic feet of gas took up 23.2 grains of the naphtha, whilst the last 450 cubic feet only took up 7.3 grains. Another difficulty found was the increase of evaporation with the rise in the temperature of the gas, as with an ordinary form of carburetter exposed to atmospheric changes, the en-

richment of the gas, which reached 54.4 per cent in summer with an average temperature of 22° C., fell in winter to only 22 per cent with an average temperature of 3° C. Of course, in these carburetters a good deal depended upon the form of apparatus; and it was found, on trying different shapes with the same naphtha, that when the gas merely flowed through a box containing a layer of it, only about 3.2 grains were taken up; while with a carburetter in which the naphtha was sucked up by cotton fibre, so as to expose a large surface to the gas, as much as 22 to 23 grains were absorbed. One of the most important points noticed during these experiments was, that it was only a poor gas which could be enriched in this manner, and that if a rich cannel gas was passed through the naphtha, it became robbed of some of its illuminating power.

It must be clearly borne in mind, in approaching this subject, that the evaporation of a hydrocarbon into a permanent gas—i.e., a gas which does not liquefy within the ordinary range of temperature—is a question neither of specific gravity nor of boiling point, although the latter has more to do with it than the former. It is purely a question of vapour tension. Most liquids, when left to themselves in contact with the atmosphere of other gases, gradually pass into the state of vapour, and disappear; and those which evaporate the quickest are said to be most volatile. If ether, for example, is dropped upon an exposed surface, it at once disappears, and causes, by its evaporation, considerable cold; and the lightest forms of naphtha do the very same thing. But although this evaporation takes place with rapidity with liquids of low boiling-point, it must not be forgotten that even many solids have the same property—naphthalene, camphor, and iodine being cases in point. It must also be remembered that evaporation occurs over a very wide range of temperature; but that for each substance there is a limit below which evaporation does not seem to take place. So that, when considering the suitability of a liquid for carburetting in this way, it is far more important to determine its vapour tension than its specific gravity or its boiling-point.

So far, all systems for carburetting gas with liquid hydrocarbons at the burner have proved failures, but in the Albo-Carbon light the vapour of naphthalene is caused to mingle with the gas just before combustion, the volatilisation being effected by a spur of metal heated by the flame itself, which conducts the heat back into a chamber containing solid naphthalene, through which the gas passes, and this process has proved very successful.

Any system to be generally adopted must be applied to the gas in bulk before distribution. In doing this there are two factors to be considered—the vapour added must be in such proportion to the gases which have to carry them that no fear need exist of their being deposited by any sudden cooling of the gas; and care must be taken that the vapour added is not in sufficient quantity to throw out of suspension the volatile hydrocarbons in the gas. The carrying power of a gas depends upon its constituents; for in the same way that liquids vary in their power of dissolving and carrying—i.e., keeping in solution—solids, so do gases vary in their power of bearing away the more volatile hydrocarbons. If the carrying power of air is taken as unity, then the power of ordinary coal gas is about 1.5, while hydrogen would be nearly 3.5; and it is manifest that attention must be paid to the ratio of the constituents present, if gases of varying composition are to be carburetted to the same degree.

During the past few months the idea of the possibility of carburetting coal gas in bulk has again been revived by the construction of an extremely ingenious apparatus, the outcome of the combined engineering skill and practical experience of Messrs. Maxim and Clark, which obviates, to a very great extent, the difficulties which arose with the older forms of carburetter. It has been shown that, when carburetting a gas with a gasolene or light naphtha spirit, the more volatile portions enrich the gas to an

* Abstract of the Cantor Lectures delivered at the Society of Arts. Communicated by the Author.

undue extent at first, and that as the process continues, the amount taken up becomes gradually less. This would not so much matter in carburetting the gas in bulk before it went into the holder, as it would become to a great extent mixed by diffusion, and a gas of fairly even illuminating power would result; but the Maxim-Clark apparatus is intended not only to do this, but also to carburet the gas used in large establishments and works.

This apparatus is of such a form that in small installations the whole of the gas to be used can be passed through and each portion supplied with its own share of hydrocarbon; whilst, when carburetting gas in bulk, a certain portion can be withdrawn from the main, carburetted, and again returned to the main, where mingling with the steady flow of gas, the whole becomes of uniform composition.

In the earlier days of the gas industry, attempts were made to utilise tar for the production and enrichment of gas; and the patent literature of the century contains many hundred such schemes, most of them being still-born, while a few spent a short and sickly existence, but none achieved success. The reason of this is not difficult to understand. In order to make gas from tar, two methods may be adopted—either to condense the tar in the ordinary way, and afterwards use the whole or portions of it for cracking into a permanent gas; or to crack the tar vapours before condensation by passing the gas and vapours through superheaters. If the first method is adopted, the trouble which at once presents itself, and in a few hours brings the apparatus to grief, is that tar contains 60 per cent of pitch, which rapidly chokes and clogs up all the pipes; while if an attempt is made to use a temperature at which the pitch itself is decomposed, it is found that a non-luminous or very poorly luminous gas is the result, and that a heavy deposit of carbon remains in the superheater and retort, and even at high temperatures easily condensable vapours escape, to afterwards create trouble in the pipes.

The most successful attempt to utilise certain portions of the liquid products of the distillation of coal is undoubtedly the Dinsmore process, in which the coal gas and the vapours which, if allowed to cool, would form tar are made to pass through a heated chamber, and a certain proportion of otherwise condensable hydrocarbons are thus converted into permanent gases. Using a poor class of coal, it is claimed that 9800 cubic feet of 20 to 21 candle gas can be made by this process; while by the ordinary system, 9000 cubic feet of 15-candle gas would have been produced.

In distilling the coal in the ordinary way, the yield of tar is 11 gallons per ton; but by the Dinsmore process, only seven gallons. On examining the analysis of the ordinary and Dinsmore tar, it is at once evident that the 4 gallons which have disappeared are the chief portions of the light oils and creosote oil; and these are the factors which have given the increase of illuminating power to the gas.

In enriching a poor coal gas by injecting paraffin oil into the retort during distillation, it must be borne in mind that, as the coal is undergoing distillation, in the earlier stages a rich gas is given off, while towards the end of the operation the gas is very poor in illuminants and rich in hydrogen; the methane disappearing with the other hydrocarbons, and the increase in hydrogen being very marked. Mr. Lewis T. Wright employed a coal requiring six hours for its distillation, and took samples of the gas at different periods of the time. On analysis, these yielded the results given in Table.

This may be regarded as a fair example of the changes which take place in the quality of the gas during the distillation of the coal. In carburetting such a gas by injecting paraffin into the retort, it would be great waste to do so for the first two hours, as a rich gas is being given off which has not the power of carrying a very much larger quantity of hydrocarbons—being practically saturated with them. Consequently, to make it take along

Time after commencement of distillation.

	10 m.	1 h. 30 m.	3 h. 25 m.	5 h. 35 m.
Sulphuretted hydrogen	1'30	1'42	0'49	0'11
Carbon dioxide	2'21	2'09	1'49	1'50
Hydrogen	20'10	38'33	52'68	67'12
Carbon monoxide	6'19	5'68	6'21	6'12
Marsh gas	57'38	44'03	33'54	22'58
Illuminants	10'62	5'98	3'04	1'79
Nitrogen	2'20	2'47	2'55	0'78

with it, in a condition not easily deposited, any further quantity, the paraffin would have to be broken down to a great extent; and the temperature necessary to do this would seriously affect the quality of the gas being given off by the coal. When, however, the distillation had gone on for three hours, the rich portions of the coal gas would all have distilled off, and the temperature of the retort would have reached its highest point; and this would be the time to feed in the oil, as its cracking being an exothermic action, the temperature in the retort would be increased, and the gas rich in hydrogen which was being evolved would carry with it the oil gas, and prevent any re-deposition.

ON DETERMINING THE SENSITIVENESS OF PHOTOGRAPHIC PLATES BY MEANS OF THE SPECTROGRAPH.*

By Professor VICTOR SOHUMANN.

As long as photographers employ exclusively collodion or gelatin plates, sensitive only for blue and indigo and, to a limited degree, to ultra-violet rays, their relative sensitiveness can only be found by a series of objective exposures, or by means of any of the sensitometers proposed for practical use during the last decade. None of these instruments has become so popular as that constructed by Warnerke, and many plate manufacturers state with its aid the numerical sensitiveness of their wares. Notwithstanding the limited efficacy of the instrument, and the want of reliability of its luminous plate, practice has proved it to be not deceptive enough to lead to entirely useless results. This refers, of course, to the ordinary plate only.

Of late, however, when the relations of absolute sensitiveness have been entirely changed by the introduction of orthochromatic methods, the advantages offered by the Warnerke sensitometer have become seriously sceptical, not only in abstract scientific examination but also to a very great extent in practical working. The reason of that is simply an insufficiency of light rays radiating from its phosphorescent plate. It is of a light blue colour and homogeneous to all appearances; any other rays I have not yet been able to detect. To be fully convinced of this fact I have adopted a method of investigation, much safer unquestionably than any other heretofore proposed. After making the plate luminous in the ordinary manner it is covered with a card, in the centre of which is cut a slit of 2×30 m.m. dimensions. The rays passing through it, when examined by means of a prism, show the whole spectrum to consist of a single band only, equal in colour as well as width to the luminous slit, as far at least as ocular observation goes, but neither yellow nor red is perceptible. No other light but blue is radiated from the luminous plate; not perfect blue, however, it is of distinct tone. Supposing, then, a photographic plate, not at all sensitive for this particular ray, were examined with the Warnerke sensitometer, the test for sensitiveness can result only in total failure, because the plate might possibly be highly sensitive for rays other than those radiated from the luminous substance.

* Communicated by the Author.

Similar facts will be found to exist with all orthochromatic plates. They are all sensitive for blue, but likewise so for yellow and red, according to the sensitive they contain. As far as the least refrangible light rays are concerned, the Warnerke sensitometer cannot be depended upon, and the results obtained when orthochromatic plates are obtained with it are totally unreliable. If those highly sensitive plates should be generally adopted for practical work, of which not the least doubt can exist, the days of Warnerke's instrument are numbered.

To describe here other sensitometers may be well omitted; they all have been superseded by the reliable spectrograph, by the aid of which more distinct information on the sensitiveness of photographic plates is obtained. Whoever desires to learn of their relations to the action of light rays of different colours should resort to the spectrograph. Heavy flint glass, like that of the Amici prisms, should, however, be entirely excluded from the instrument; these glasses are impenetrable to ultra-violet. Violet even, and not less so indigo and blue, are held back with much energy, while the luminous rays, yellow and red, are allowed to pass through flame without any hindrance almost. Such prisms must naturally lead to erroneous sensitometer numbers. On account of partial absorption, yellow is reproduced with excessive force, and plates found to be highly sensitive for yellow and red in the spectrograph will fail to show the same properties with objective exposures.*

Lenses and prisms made of crown glass or of light flint with less dispersive power are preferable for ordinary purposes. With any camera and without much trouble a suitable spectrograph may be easily constructed. To obtain faultless spectrum photographs a scrupulously correct instrument is not necessary. I have made sharpest pictures with precision instruments as well as with apparatus but roughly built, and even professional spectroscopists have made the most astounding discoveries with improvised instruments.

To find the behaviour of plates towards any light source a series of spectra, with regularly increasing time of exposure, should be photographed, the plates dried, and be examined in regard to the time required to produce a developable impression by different colours. The different sensitiveness will then be found to be reversely proportioned to the time of exposure. Were we, for example, to inquire how the sensitiveness of a Vogel eoside of silver plate (manufactured by Prentz, of

Munich), is proportioned to our own instrument the *first spectrum of the series to be photographed should be exposed for such a short time as not to produce a developable impression*. Subsequent and longer exposure will then generally produce an image of extremely feeble character—a mere breath upon the plate. The thinner the picture of the spectrum, and the clearer ground of the plates, the more reliable is the sensitometer number derived from the series of spectrograms made by increasing time of exposure. As long as sensitiveness alone is the object of inquiry, the intensity of the plate is of no importance whatever. *It is totally wrong to determine numerical value of light-sensitive films by the density of the negative.*

Sensitiveness and intensity are two entirely different things, as every photographer knows who understands the use of the sensitometer. How little hold is offered by the intensity of the plate, when inquiring into its sensitiveness, is proved by the fact that the two never go hand in hand. Some plates resist strenuously the action of certain rays before decomposition of the light-sensitive components takes place; but when their stability has yielded at all to the force of the developer the intensity of the negative increases with much rapidity. Density builds up easily when the exposure has been longer than required for the production of the breath-like picture; not proportionately, however, but progressively. This phenomenon occurs with Vogel's eosine plates to an unusual extent. A hundred times have I had opportunity to observe these properties when associated with Dr. Zettnow, of Berlin, and to whom we are indebted for the most important researches of erythrosine plates, to examine extensive series of orthochromatic plates. Other phenomena occurring and observed by studious investigators may be well explained by this progressive increase of density, pre-eminently among them two peculiarities—the very changeable intensity of the maximum in yellow, and different yellow action even under strictly normal conditions.

Whoever wishes, with the foregoing explanation on hand, to determine the yellow and blue sensitiveness of erythrosine plates, will find that the former never reaches the height, numerically, stated by Dr. Vogel when the exposure is made by high altitude of the sun. Far from mid-day, or in winter-time, the proportions of brightness in the sun spectrum are entirely changed. The general sensitiveness of the plate advances then more and more towards the red end of spectrum. When the sun stands low, at its rise and set, the erythrosine silver plate may triumph to a still greater extent, for then it is nearly exclusively sensitive for yellow and red, but for no other rays.

THE ANALYSIS OF CUPRIC BROMIDE, AND THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Continued from p. 23).

II. FINAL DETERMINATION.

Preparation of Cupric Bromide.

In preparing cupric bromide for the final series of experiments it was decided to adopt a wholly new method, namely, the action of excess of bromine upon copper in the presence of water. Pure copper was prepared from a new source, the chemically pure sulphate from a noted German house, by the method which has so often been described.† The salt was freed from a possible trace of bismuth and iron by potassic hydrate in very dilute solution, precipitated from the concentrated filtrate by sul-

* To understand clearly the great influence of partial absorption produced by Amici prisms compare my spectrograms of erythrosine silver (David and O. Scolik; Die orthochromatische Photographie. Knapp; Halle a/S. 1890) with those of Vogel's soda-eosine silver plates (his Handbuch der Photographie, 4th Ed., 1890.) Both photographs illustrate the sensitising action of one and the same dye, for erythrosine is identical with soda-eosine. Vogel made his spectrum photographs with a spectrograph furnished with an Amici prism; mine was made with the large Quartz spectrograph. Vogel's prism has swallowed up the ultra-violet so completely that not a trace of it is discernible; and how much the action of indigo and blue has been suppressed may be judged of by the high intensity of the maximum in yellow, according to Vogel's own calculation of six and even ten times force, and as impenetrable as the blue maximum. No erythrosine plate has this enormous sensitiveness for yellow, unless it be exposed under abnormal conditions. But when colour-sensitive plates are exposed in the gloom of an Amici prism, and the sombre light filtered through the terrestrial atmosphere, and when the sun is at its lowest altitude (the first days of January), it is quite easy to demonstrate ocularly a high sensitiveness for yellow, that under no other conditions is possible to attain. Furthermore are the ideas of intensity and sensitiveness sadly confused, ostensibly with a purpose—that of shedding lustre upon the eosine-silver plate for a long time to come. Of quite a different character are my erythrosine silver spectrograms. They are distinguished by powerful action in ultra-violet, an intense violet and a vigorous blue. Astonishing is the much lower yellow sensitiveness of my plates when compared with the action of blue on the one side and with the Vogel spectra on the other. Had I placed before the slit of my instrument a heavy flint, like an Amici prism, and had I exposed my plates when the sun stands low, when the refrangible rays of the spectrum half act with little energy, my spectrograms would have been equal to Dr. Vogel's. But I preferred to show how erythrosine silver behaves under normal conditions. Errors in the photographing of my spectra, and upon which the difference of time and Dr. Vogel's might be based, are improbable. Researches made at other times and occasions have invariably led to the same results.

* Contributions from the Chemical Laboratory of Harvard College. —From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxv.

† *Proceedings of the American Academy of Arts and Sciences*, xxii., 346; xxiii., 178; see ante.

phuric acid, and after many re-crystallisations was finally twice successively decomposed by fractional electrolysis. The resulting copper was a very brilliant and beautiful substance; after being thoroughly washed and dried at 90°, it showed no trace of oxidation on standing three months.

The problem of the preparation of pure bromine has been admirably solved by Stas,* and the method adopted in the present case was largely based upon his, although differing from it in several important particulars. Sixty grms. of potassic bromide in dilute solution were completely freed from a trace of iodine by two additions of a small quantity of bromine water, shaking out each time with successive portions of pure carbon disulphide until the two liquids in the separating funnel were alike colourless. After evaporation the aqueous solution of potassic bromide was mixed with pure dilute sulphuric acid and pure powdered manganese dioxide, and the mixture was subjected to distillation from a glass retort over a water-bath into a glass condenser packed in ice. The manganese dioxide had previously been washed with an aqueous solution of bromine, pure water, hot dilute sulphuric acid, and finally with pure water again until neutral to litmus.

Thirty-seven grms. of bromine thus prepared were washed twice with water and distilled four times in two very small flasks with long side tubes, the bulbs being alternately packed in ice and immersed in hot water as they alternately served for condenser and retort. The neck of the one serving as the latter was stopped with a glass rod wrapped in fine asbestos, and this bulb was always cleaned and dried before being in its turn used as condenser. In this way bromine may be indefinitely re-distilled with very little escape of vapour and without the least inconvenience.

The resulting bromine, although free from iodine, of course still contained an impurity of chlorine, which it is possible to remove by the solution of the whole mass in concentrated aqueous calcic bromide. The required salt was made by the addition of bromine to a mixture of milk of lime with sufficient ammonia water to prevent the formation of oxygen salts of calcium. The clear filtrate from this operation was evaporated to dryness, and the slight excess of lime was neutralised by means of pure hydrobromic acid. The calcic bromide thus formed was freed from iodine in the manner described in the case of the potassium salt, and a very small amount of the pure product served to dissolve all the bromine previously made. The intensely coloured heavy solution parted with some of its bromine on dilution, and with nearly all the remainder on gentle distillation.

Bromine thus prepared is absolutely free from chlorine as well as from iodine. After being twice more distilled, it was taken at once for the preparation of the bromide of copper used in the final determinations of the atomic weight. The combination of the halogen and the metal took place in a cooled flask containing water, and after its completion the slight excess of bromine—added to insure absence of cuprous bromide—was expelled by gentle evaporation to dryness in a glass dish. The nearly normal cupric bromide was then dissolved in a small amount of water, and the strong solution filtered through asbestos in a perforated crucible.

All experiments hitherto tried upon the salt had led to the conclusion that the solid alone loses bromine in the air, the solution being perfectly stable. If, therefore, it were possible suddenly to crystallise the salt and immediately to wash and dissolve it, we might hope to obtain a normal solution by a method which would insure perfect purity. This result was at last attained by the concentration of the dissolved cupric bromide, barely acidified with pure hydrobromic acid, to the consistency of syrup—the containing vessel being left wholly undisturbed in vacuo for thirty-six hours. Upon agitation and

cooling with ice, the resulting odourless, black super-saturated solution at once crystallised into a mass of brownish green needles, which were collected on a perforated crucible and washed three times with a very little water. These needles were wholly different in form and appearance from the black scales previously prepared: they were undoubtedly identical with those described by Berthelot and Lowig.† The dilute solution of these crystals deposited only a wholly insignificant amount of the basic bromide upon standing, and this small amount was undoubtedly formed by the rapid current of air drawn through the Gooch crucible. After remaining for more than a week longer there was no sign of further deposition, and the pure liquid was subjected to analysis, with the results given below.

Method of Analysis.

The copper was determined in the same manner as before, except that in experiment 18 the crucible serving as the negative electrode was previously coated inside with a thin film of copper, so that the external conditions before and after the analysis might be the same. The data of this experiment may perhaps make the understanding of the method more clear.

Experiment 18.

	Grms.
Weight of glass-stoppered flask with CuBr_2 solution	93.872
Weight of glass-stoppered flask alone ..	32.289
„ solution taken	61.583
	Corrected wts
	Grms.
Crucible with copper before analysis ..	36.5516
1st drying crucible with additional Cu after analysis	37.2260
2nd drying crucible with additional Cu after analysis	37.22605
Gain of copper film	0.6744
Correction to vacuum	0.0000
Weight of copper found	0.6744

Result.

Weight of copper in 50 grms. solution =	
$\frac{50 \times 0.6744}{61.583}$	0.54755

In precipitating the bromine from new portions of the solution, not only was the resulting silver bromide weighed, but also the silver required to form it; and this last value was determined according to two distinct methods. In the first place, the weight of silver required for a given weight of the copper bromide was calculated, and somewhat less than this amount was weighed out and dissolved in nitric acid in the manner before described. The cupric bromide was then cautiously added to the warm dilute solution, and the deficiency of silver made up by very careful titration with a solution containing one gm. of silver to the litre.‡ After noting carefully this first value for the amount of silver required, a slight known excess of the standard solution was added, and the silver bromide was washed, collected, and weighed upon a perforated crucible as before. The excess of silver in the filtrate was now carefully determined by means of a standard solution of ammoniac sulphocyanide, using as a standard of colorimetric comparison solutions containing an equivalent amount of pure copper nitrate and small known amounts of silver nitrate. This second method of determining the amount of silver required to precipitate the bromine is not so accurate as the first, but is of value

* Berthelot and Lowig, *loc. cit.*

† Stas's "Untersuchungen," p. 158; Uebergesetzt von L. Aronstein, Leipzig.

‡ For a further description of the method by Prof. J. P. Cooke, see *Proceedings of the American Academy of Arts and Sciences*, xvii., 28

(To be continued).

The Determination of Zinc in Ores.—**Delio Coda.**—The author dissolves 2·5 grms. zinc ore in 15 to 20 c.c. of aqua regia, evaporates to dryness, adds 15 to 20 c.c. sulphuric acid, and heats again until the white vapours of sulphuric acid show that all nitric and hydrochloric acid have been expelled. If copper, cadmium, &c., are present the liquid is diluted, and these metals are precipitated by means of sulphuretted hydrogen and filtered off. The filtrate is boiled until the sulphuretted hydrogen is expelled; if only lead is present it is sufficient to dilute the solution with water and to filter. To the filtrate which contains only iron, zinc (manganese and alkalies) ammonia is added to neutrality, and 40 c.c. ammonia in addition, containing $\frac{1}{2}$ ammonium carbonate. The iron falls at once without carrying zinc oxide along with it. After the flask has become cool it is filled with water up to 500 c.c., and filtered through a dry, folded filter. Three portions of 100 c.c. each are taken from the filtrate, and each is diluted to 250 c.c. Each portion consequently contains the zinc of 0·5 gm. ore, and the solution thus obtained is ready for titration. The standard liquid is prepared by dissolving a known quantity of pure zinc in 4 c.c. hydrochloric acid; the quantity of zinc should be approximately equal to that which is supposed to be present in 0·5 gm. of ore. The solution is diluted, rendered alkaline with 20 c.c. ammonia, and again diluted to 250 c.c. For precipitating the zinc from the standard liquid and from the solution the author uses a graduated Mohr's burette, containing a 2 per cent solution of sodium sulphide. As indicator there is used an 8 per cent solution of sodium nitro-prusside, which is placed upon a perfectly dry porcelain slab in drops of about 5 m.m. each. When the zinc has been almost perfectly precipitated in the two solutions by sodium sulphide, the zinc sulphide is let settle until a transparent layer appears above the precipitate. A little of this clear liquid is taken up with a pipette and some of it is let fall upon one of the drops of nitro-prusside until the drop is 30 m.m. in diameter. If the well-known red colour does not appear (which would indicate the presence of free alkaline sulphide) $\frac{1}{4}$ c.c. of solution of sodium sulphide is added to each solution, which is then shaken, let settle, and the operation repeated until the red colour appears upon the tile. If one of the

liquids has a fainter colour than the other an attempt is made to get the same shade by adding quantities of one-tenth c.c. sodium sulphide. If the known weight of zinc in the standard liquid is called *a*, the c.c. of solution of sodium sulphide required to throw down the pure zinc, *b*, and those used for the solution of the ore *c*, then the percentage of zinc in the ore is—

$$\frac{200 \cdot a \cdot c}{b} \text{ per cent.}$$

In order to determine the accuracy of this process the iron precipitate was analysed after being carefully washed with ammoniacal water. It contains not a trace of zinc, but 3.5 per cent of its weight of ammonium sulphate. But if no ammonium carbonate is added to the ammonia or 10 per cent of zinc is lost.

Nitrogenous Bases in the Products of Alcoholic Fermentation.—E. C. Morin.—From the *Comptes Rendus*.

Action of Air and Heat upon the Tannin of Willow Bark.—W. Sonne and F. Kutscher.—This form of tannin is partially decomposed if its aqueous solution is heated or concentrated.

Notes on Kjeldahl's Determination of Nitrogen.—Schönherr (*Chemiker Zeitung*) and Sangerod (*Arch. de Pharmacie*) recommend the determination of the ammonia formed by means of the azotometer. A. Devarda recommends Jodlbauer's modification of the original process. Lindot (*Comptes Rendus*) obtains good results with the Kjeldahl process in determining nitrogenous bases in alcoholic liquids. Poporic prefers the Kjeldahl method to that of Varrentrap and Will in determining nitrogen in tobacco.

Determination of the Neutralising Power of Acids.—F. Fuchs (*Akademie in Wien*).—The author employs the action of the acids upon the alkaline sulphohydrates.

On the Oxybenzoic Acids and on Benzoic Acid.—Oechsner de Coninck (*Chemiker Zeitung*).—Meta- and para-oxybenzoic acids can be determined by the cautious evaporation of their solutions in ethyl and methyl alcohols. Salicylic acid can be determined in their solutions in ethyl and methyl alcohol, acetone, &c., by a gradual evaporation with the aid of the water air-pump. Meta- and para-oxybenzoic acids can be determined by the slow evaporation of their aqueous solutions. Salicylic acid begins to sublime between 80° and 85°; both its isomers require higher temperatures. Benzoic acid begins to sublime between 45° and 50°.

Determination of the Hydroxyl Group.—C. Loring, Jackson, and G. W. Rolfe.—From the *American Chemical Journal*.

Determination of Methoxyl in Organic Compounds.—S. Zeisel.—The author utilises the well-known property of the methoxyl group (OCH₃) to form iodomethyl with hydriodic acid. As iodomethyl is decomposed by an alcoholic solution of silver nitrate with elimination of silver iodide, we have the means for a quantitative determination of methoxyl. Rudolf Benedikt and Anton Grüssar recommend the application of Zeisel's process for testing fats, resins, ethereal oils, &c. They have examined an entire series of ethereal oils by this method, and calculated the values obtained as methyl originally present. They call the percentage thus obtained the "methyl-number," remarking that ethyl and the higher alkyls appear also expressed as methyl.

A New Method for the Quantitative Examination of Saccharine.—J. Remsen and W. M. Burton.—From the *American Chemical Journal*.

Detection and Determination of Yolk of Egg.—S. Bein (*Berichte der Deutsch. Chem. Gesellschaft*).—See page 11.

Detection of Copper in Wine.—T. Gigli (*Orosi and Chemical Centralblatt*).—The author steeps a galvanic

element (zinc and platinum) in the wine, which is first acidified with hydrochloric acid. The plates are 8 c.m. long, 0.8 c.m. wide, and connected with each other at one end by means of a platinum wire, which also serves to suspend the element to a glass rod. In carrying out the test, 1 litre of wine is mixed with 20 c.c. hydrochloric acid at specific gravity 1.15, the liquid is divided into 5 parts, and an element is suspended for 24 hours in each portion. The copper present is deposited upon the platinum.

Examination of Whiskey.—Clifford Richardson.—From the *American Chemical Journal*.

A Chemical Reaction for the Bacteria of Cholera.—It is known that cultures of the bacillus in question are coloured red by hydrochloric acid. R. Pfeiffer (*Zeit. f. Hygiene*) states that this reaction is also produced by cultures of another comma-bacillus, *Vibrio metschnikoff*.

Examination of Beet Sugar for Inverted Sugar, Dextrine, &c.—Ihl (*Chemiker Zeitung*).—The author adds a solution of methylene blue, which is decolourised by the impurities in question.

A Process for Detecting Colouring Matters.—Gaston Dommergue.—From the *Moniteur Scientifique*.

The Use of the Kjeldahl-Willarth Nitrogen Process for Investigations on the Transformations of Matter.—Argutinsky (*Pflüger's Archiv*).—The author is satisfied with the results.

New Process for Determining Uric Acid.—Arthand and Butte (*Comptes Rendus Soc. de Biologie*).—The process is founded on the insolubility of cuprous urate, the phosphates present being first removed by means of sodium carbonate.

Detection and Determination of Sugar in Animal Fluids.—Fr. Schenck (*Pflüger's Archiv*).—The author comes to the conclusion that glucose is capable of combining with the albumen of blood.

Detection of Albumen in Urine.—Const. Zouchlos (*Vienna Med. Zeit.*).—A solution of mercuric chloride produces in albuminous urines a distinct turbidity, which does not disappear on adding acetic acid. A mixture of 1 part acetic acid with 6 parts of a 1 per cent solution of mercuric chloride precipitates albumen, but not peptone, uric acid, or phosphates.

Journal de Pharmacie et de Chimie.
Vol. xxii., No. 1.

On the Influence of Different Fruit-Ferments upon the Aroma of Fermented Liquors, and on the Production of Cider from Barley.—Georges Jacquemin.—Already noticed.

Improvement in the Manufacture of Soda, Potassa, and Chlorine.—W. P. Thompson.—An English patent, No. 13306, 1888.

Preparation of Metallic Manganese by Means of Manganese Chloride and Magnesium.—E. Glatzel.

Improvements in the Manufacture of Alkalies, Alkaline Salts, and Chlorine from Sodium and Potassium Chlorides.—T. Parker and E. Robinson.—An English patent, No. 14799, October 3rd, 1888.

Process for Detecting Wood-Paper.—M. Wurster.—The following reagents serve to distinguish wood-paper from pure cellulose:—

Reagent.	Wood-paper.	Cellulose.
Orcine	Dark red	Nothing.
Resorcine	Deep green	Violet.
Pyrogalllic acid ..	Blue-green	..
Phenol	Yellow-green	..
Phloroglucine ..	Blue violet	Nothing.

The presence of wood in paper can be detected and the quantity even estimated by means of dimethyl paraphenyldiamine.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Vol. v., No. 58.

Report Presented by M. le Chatelier on M. Candlot's Memoir concerning the Properties of Cement.—M. Candlot, discussing the action of sea-water on cements, proves that of the three principal salts present, sodium chloride exerts no influence. Calcium chloride in dilute solutions (20 grms. per litre), retards the setting of cement just as does sea-water, whilst solutions at 300 grms. per litre cause a considerable acceleration. He further shows that the reason why weak solutions of calcium chloride retard setting is because they prevent the solution of the alumina of the calcium aluminates. Concentrated solutions of calcium chloride, on the contrary, increase the solubility of the aluminates and even of the ferrites. This increase of the solubility of alumina, the direct cause of the acceleration of the setting, results from the formation of the calcium chloro-aluminate.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xi., No. 3.

This issue does not contain any chemical matter.

MEETINGS FOR THE WEEK.

- MONDAY, 19th.**—Medical, 8.30.
Society of Chemical Industry, 8. "On the Constitution of Butter" (Illustrated by Specimens), by J. Alfred Wanklyn. "Some Experiments on the Cyanide Process for the Extraction of Gold from Low Grade Gold Ores," by T. Graham Young and Watson Smith.
- TUESDAY, 20th.**—Institute of Civil Engineers, 8.
Pathological, 8.30.
Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley, F.R.S., B.S., F.R.C.S., Fullerian Professor of Physiology, R.I.
- WEDNESDAY, 21st.**—Society of Arts, 8. "Photography in Aniline Colours," by A. G. Green, C. F. Cross, and E. J. Revan.
Meteorological, 7. (Anniversary).
Geological, 8.
Microscopical, 8. (Anniversary).
- THURSDAY, 22nd.**—Royal, 4.30.
Royal Society Club, 6.30.
Institute of Electrical Engineers, 8.
Society of Arts, 4.30. (Indian Section). "Hall-Marking of Silver Plate, with Special Reference to India," by Edward J. Watherston.
Royal Institution, 3. "The Little Manx Nation," by Hall Caine.
- FRIDAY, 23rd.**—Royal Institution, 9. "Some Applications of Photography," by The Right Hon. Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.
- SATURDAY, 24th.**—Royal Institution, 3. "Pre-Greek Schools of Art," by W. Martin Conway, M.A., F.S.A.

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THE CHEMICAL NEWS.

VOL. LXIII. No. 1626.

ON WOLF AND RAYET'S BRIGHT-LINE STARS IN CYGNUS.*

By WILLIAM HUGGINS, D.C.L., LL.D., F.R.S.,
and Mrs. HUGGINS.

(Concluded from p. 30).

DR. COPELAND, during his travels in the Andes in 1883, observed γ Argus, and five small stars with bright lines in their spectra. He says:—"As far as my measures and estimates go, all of them belong to the same class as the three Wolf-Rayet stars in the Swan, to which Professor Pickering has since added a fourth outlying member."†

Dr. Copeland gives the position of the bright blue band in γ Argus as λ 464'6.

Among the stars in the great cluster G.C. 4245, near ζ Scorpii, Dr. Copeland found a star, P. XVI. 204=Stone 9168, which has a similar spectrum, namely, with a bright band in the blue and two in the yellow. He found the position of the blue band to be λ 465'1.

In the case of two other small stars with similar spectra, he found respectively for the blue band the approximate measures λ 463'3 and λ 463'6.

These four stars were similar, therefore, at the time of the observations to No. 4013 and No. 3956, in which the maximum of the blue band is not far from λ 464, and therefore outside and beyond the ordinary visible limit of the blue carbon band.

Professor Vogel observed two other stars with similar spectra, of which the main feature is the very bright band in the blue region, namely, Arg. Oeltzen 17681 and Lal. 13412. These stars are too low in southern declination to be reached from our observatory.

Vogel places the blue band in Lal. 13412 at λ 469, which shows that it has a position similar to that of No. 4001 and of Dr. Copeland's star. In the case of Arg. Oeltzen 17681, Vogel makes the band to extend through about the entire range of refrangibility occupied by the two positions of the blue band in the Wolf-Rayet stars according to his measures of them, namely, from λ 461 to λ 470, with a maximum at the place where they would overlap, namely, λ 466.

Let us consider the four stars with an intensely brilliant blue band which we have examined; in two of them the band extends from about λ 464 to λ 467, and in the other pair the band has a less refrangible position, from about λ 466 to λ 471, but there is also in the case of each pair a very faint band visible, or suspected, at the position of the blue band in the other pair. Further, in Arg. Oeltzen 17681, Vogel found the bright band sufficiently long to include both positions of the band.

One suggestion which presents itself is whether these bands, or, more correctly, these groups of bright lines, may be variable, so that, under certain conditions, one or other of them becomes brilliant. Such a state of things would reconcile our observations of $+37^{\circ}$ 3821 with the earlier measures of Dr. Copeland, and, indeed, might possibly explain, if this variability should be established, the circumstance that so accurate an observer as Professor Vogel did not detect, even with his smaller instrument in 1873, the very large difference of position of the band in 4001 from that of the corresponding band in the stars 4013 and 3956, which was so conspicuous in

1883, and is so still at the present time. In the broad characters of their spectra, and in their magnitudes, the Wolf-Rayet stars have remained unchanged since the discovery of their remarkable spectra in 1867.

As the only direct evidence of such a variability rests upon the change of position of the band in Dr. Copeland's star since his observation of it in 1884, I wrote to Dr. Copeland to ask if his position rested upon sufficiently accurate measures or was arrived at by estimation only. In reply, he says:—"The place of the blue line (rather, band) in D.M. $+37^{\circ}$ 3821, given in the *Monthly Notices*, is a mere estimate to show the character of the star."

Whether any change of position of the band has taken place must therefore remain at present uncertain; but, independently of any such direct evidence of variability, the two positions of the very bright blue band, with the suspicion of faint bands at the alternate positions, appear to us suggestive of possible variation, especially when we consider that the spectra of these stars consist of numerous absorption bands and groups of bright lines upon a feeble continuous spectrum, a character of spectrum which seems to point to a probably unstable condition of the atmospheres of these stars.

The large difference of position of the bands in the two groups of stars is much too great to admit of an explanation founded upon a possible orbital motion of the stars. Besides, the near coincidence of Dr. Copeland's measures of two bright lines common to the stars 4001 and 4013 shows that the difference of position of the blue band is not due to motion in the line of sight.*

If future observations should show that the bright blue groups are variable, we must look, it would seem, to causes of a physical or a chemical nature.

If the two bright groups, differing in position by about λ 0040, belong to different substances, or, less probably, perhaps, to different molecular conditions of the same substance, it is conceivable that one or other substance, or molecular state, may predominate and appear brilliant, according to certain unknown conditions which may prevail in the star's atmospheres.

It might be suggested that both bands are due to a long group of bright lines extending from about λ 461 to λ 471, and that this long group is cut down by absorption bands; in one pair of stars an absorption from the green cuts off the less refrangible part of the long group down to about λ 467, while in the other two stars the more refrangible part is eclipsed, and the bright group appears as in 4001.

The appearance of the spectra in our instruments scarcely seems to us to be in accordance with such a view, because, though we did suspect brightenings in the alternate places, the appearance of the spectrum was not such as to suggest a bright group dimmed by absorption, for in that case the amount of absorption needed to all but obliterate a group, as bright as it appears in the other pair of stars, would have blotted out completely the relatively feeble continuous spectrum. This continuous spectrum, though faint, was still distinctly seen.

More observations are needed, but it appeared to us desirable by these suggestions to invite the attention of observers to the points in question.

As the main object of our examination of these stars was to determine whether the bright band in the blue was to be regarded as showing the presence of carbon by its coincidence with the blue band of the hydrocarbon flame, we were not able, from the pressing claims of other work, to extend our examination to many other

* Dr. Copeland permits me to give the following measures of the bright lines in the Wolf-Rayet stars, which were made by him and Mr. Lohse on January 28, 1884:—

Star.	1st yellow line.	2nd yellow line.	Bright line.	Faint line.	Large blue band.
$+35^{\circ}$ 4001..	—	—	541'2(3)	522'0(1)	469'5(3)
$+35^{\circ}$ 4013..	582'4(2)	568'9(2)	541'0(2)	—	465'4(2)
$+36^{\circ}$ 3956..	581'0(2)	570'4(2)	—	543'3(1)	464'9(2)

* From the Authors. A Paper read before the Royal Society, Dec., 1890.

† "An Account of some recent Astronomical Experiments at High Elevations in the Andes," *Copernicus*, vol. iii., 1883.

points in connection with the spectrum of these faint stars, for an exhaustive examination of which, indeed, our instruments are not sufficiently powerful.

We have stated already that the fairly luminous continuous spectrum reaches up to the bright band in all three stars, and extends beyond into the violet, as far as the eye could be expected to follow it.

The spectra are weakened at many points by what appear to be absorption bands, and are crossed by several brilliant lines, the positions of some of which have been given by Vogel and by Copeland.

An examination with spectroscope B of some of these bright lines, as they appear under small dispersion, showed them to be really not single lines, but short groups of closely adjacent bright lines.

One of the brightest of these lines is found in the star No. 4013, at the position, according to Vogel, of λ 570.

Dr. Copeland's measure for this line is λ 568.9 in star 4013, and λ 570.4 in the star 3956.

As this position is not very far from that of the green pair of sodium lines at λ 5687 and λ 5681, it has been suggested that the line in the star is due to sodium, though there is no line of comparable brightness in the star's spectrum at the position of the dominant pair of the sodium spectrum at D.*

On confronting in spectroscope B the star line with the green sodium lines, the bright space in the star's spectrum was seen to consist of a short group of several bright lines close together, and nearly equally bright. This group appeared to extend through about four times the interval of the sodium pair, which would make the length of the group about λ 0024. The green sodium lines cross the group at about one-fourth to one-third of the length of the group from its more refrangible end. The group in the star is rather less bright at the two ends, but there is no gradual shading off in either direction, as in the case of a fluting.

When we examined this part of the spectrum with the small dispersion of a prism of 45° , we were pretty sure of a feeble bright line, less refrangible than the pair of bright groups in the yellow, and not far from the position of D. We were not able to see this line in spectroscope B with sufficient clearness to enable us to fix its position. It may be D, or, perhaps more probably D₃.

In No. 4001, Vogel saw a line at the position of the F line of hydrogen. It is probable that this line, as is the case in so many stars in which it appears bright, is variable, as we were not able to see it when the H β line from a vacuum tube was thrown in. In the similar star D.M. +37° 3821, as we have stated already, the F line of hydrogen was very bright.

We were unable to detect in any of the stars a brightening of the spectrum at the position of the chief line of the bright-line nebulae. For this examination, the lead line at λ 5004.5 was thrown in, and the continuous spectrum of the star near to this position carefully scrutinised.

In their original paper, Wolf and Rayet state that they were not able to detect any nebulosity about the stars. They say:—"Elles ne présentent non plus aucune trace de nébulosité" (*loc. cit.*, p. 292).

In a recent paper, Mr. Keeler, the Lick Observatory, confirms this view. He says:—"At my request, Mr. Burnham and Mr. Barnard examined the Wolf-Rayet stars in Cygnus for traces of surrounding nebulosity, but with only negative results."

Notwithstanding these negative results, it appeared to us of great interest to ascertain further if any nebulosity would come out in a photograph of the stars taken with a long exposure.

* The 570 line is most probably the green sodium line 569, the absence of the yellow sodium being explained by the half-and-half absorption and radiation mentioned in the discussion of the causes which mask and prevent the appearance of a line in a spectrum (Bakerian Lecture for 1888, *Roy. Soc. Proc.*, vol. xliv., p. 41).

Mr. Roberts responded at once to our wish when we asked his invaluable assistance, and on November 1st, 1890, he took a photograph of this region of Cygnus, with an exposure of two hours.

The three stars come out strongly upon the plate, but there is no nebulosity to be seen near any of them. There are faint stars in close proximity to the three stars, and apparently surrounding them, and, in the case of No. 3956, six of these faint stars are seen close to it, in an apparent spiral arrangement.

Though this surrounding of faint stars should be pointed out, it should, at the same time, be stated that the whole neighbouring region is so densely studded with similar faint stars that it would be rash, perhaps, at present to suggest that this apparent connection of the bright-line stars with faint ones near them may be other than accidental.*

Professor E. C. Pickering informs me "that photographs have been obtained at the Harvard College Observatory of all the stars hitherto discovered whose spectra consist mainly of bright lines and are of the class discovered by Rayet. Part of these have been photographed at Cambridge, and the remainder in Peru." He states that they may be divided into three sub-classes, according to the characters of the bright lines. He says, further:—"Photographs of the spectrum of fifteen planetary nebulae have also been obtained. They resemble closely the spectra described above, except that the line 500 is strongly marked; 470 is seen in most of them, while the lines due to hydrogen are also bright."

It would seem that Professor Pickering's photographs do not permit him to distinguish the different positions of the bright blue band in some of these stars, for he gives for all the stars the same position, namely, λ 470.

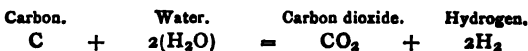
We regret that the insufficiency of our instrumental means has left our examination of the spectra of these stars less complete than we could wish. Our observations appear to us, however, to be conclusive on the main object of our enquiry, namely, that the bright blue band in the three Wolf-Rayet stars in Cygnus, and in D.M. +37° 3821, is not coincident with the blue band of the Bunsen flame.

ON GASEOUS ILLUMINANTS.†

By Professor VIVIAN B. LEWES.

IV.

WHEN carbon is acted upon at high temperatures by steam, the first action that takes place is the decomposition of the water vapour; the hydrogen being liberated, while the oxygen unites with the carbon to form carbon dioxide, thus:—



The carbon dioxide so produced interacts with more red-

* [Mr. Roberts has furnished us with the following description of the stars as they appear on his photograph:—

"No. 4001 appears as a multiple star made up of one bright, two fainter, and one very faint star partly behind the others; there is also a fourth bright star close to the multiple star. The group is surrounded by at least eight faint stars within a radial distance of $\pm 86''$ of arc from centre to centre.

"No. 4013.—The photo-image of this star is made up of three stellar images touching each other in a line slightly curved. Two are bright and one faint; and there are indications of two other faint stars behind the two bright ones. This multiple image of four or five stars is surrounded by five bright and seven faint stars; all within a radial distance of $82''$ of arc measured from centre to centre of the multiple star. The multiple image measures $\pm 55''$ in length and $\pm 19''$ in breadth.

"No. 3956.—Its photo-image is $\pm 27''$ in diameter. It is encircled by three stars of lesser brightness, and six faint ones within a radial distance of $59''$, i.e., there are nine stars within a radial distance of $59''$."—Dec. 5.]

† Abstract of the Cantor Lectures delivered at the Society of Arts Communicated by the Author.

hot carbon, forming the lower oxide, carbon monoxide, thus :—



So that the completed reaction may be looked upon as yielding a mixture of equal volumes of hydrogen and carbon monoxide—both of them inflammable, but with non-luminous flames. This decomposition, however, is rarely completed, and a certain proportion of carbon dioxide is invariably to be found in the water-gas, which, in practice, generally consists of a mixture of about the following composition :—

Hydrogen	48'31
Carbon monoxide	35'93
Carbon dioxide	4'25
Nitrogen	8'75
Methane	1'05
Sulphuretted hydrogen	1'20
Oxygen	0'51

100'00

The above is an analysis of water-gas made from gas coke in a Van Steenberg apparatus. The ratio of carbon monoxide and carbon dioxide present depends entirely upon the temperature of the generator and the kind of carbonaceous matter employed. With a hard, dense, anthracite coal, for instance, it is quite possible to attain a temperature at which there is practically no carbon dioxide produced; while with an ordinary form of generator, and a loose fuel like coke, a large proportion is generally to be found. The sulphuretted hydrogen in the analysis quoted is, of course, due to the high amount of sulphur to be found in the gas coke, and is practically absent from water-gas made with anthracite. The nitrogen is due to the method of manufacture, the coke being, in the first instance, raised to incandescence by an air-blast, which leaves the generator and pipes full of a mixture of nitrogen and carbon monoxide (producer gas), which is carried over by the first portions of water-gas into the holder. The gas so made has no photometric value—its constituents being perfectly non-luminous; and attempts to use it as an illuminant have all taken the form of incandescent burners, in which thin "mantles" or "combs" of highly refractory metallic oxides are heated up to incandescence. In the case of carburetted water-gas the gas is only used as a carrier of illuminating hydrocarbon gases made by decomposing various grades of hydrocarbon oils into permanent gases by heat.

Water-gas generators can be divided into two classes: (1) Continuous processes, in which the heat necessary to bring about the interaction of the carbon and the steam is obtained by performing the operation in retorts externally heated in a furnace. (2) Intermittent processes, in which the carbon is first heated to incandescence by an air-blast, and then, the air-blast being cut off, superheated steam is blown in until the temperature is reduced to a point at which the carbon begins to fail in its action, when the air is again admitted to bring the fuel up to the required temperature; the process consisting of the alternate formation of producer gas with rise of temperature, and of water-gas with lowering of temperature.

Of the first class of generator, none, so far, have as yet been practically successful in England.

Of the intermittent processes, the one most in use in America is the Lowe, in which the coke or anthracite is heated to incandescence, by an air-blast in a generator lined with fire-brick; the heated products of combustion, as they leave the generator and enter the superheaters, being supplied with more air, which causes the combustion of the carbon monoxide present in the producer gas, and heats up the fire-brick baffles with which the superheaters are filled. When the necessary temperature of fuel and superheater has been reached, the air-blasts are cut off and steam is blown through the generator, forming water-gas, which meets the enriching oil at the top of the first superheater, called the "carburetter," and carries the

vapours with it through the main superheater, where the firing of the hydrocarbons takes place. The chief advantage of this apparatus is that the enormous superheating space enables a lower temperature to be used for the firing, which does away, to a certain extent, with the too great breaking down of the hydrocarbon, and consequent deposition of carbon.

The Springer apparatus differs from the Lowe only in construction. In the former the superheater is directly above the generator, and there is only one superheating chamber instead of two. The air-blast is admitted at the bottom, and the producer gases heat the superheater in the usual way; and when the required temperature is reached, the steam is blown in at the top of the generator, and is made to pass down through the incandescent fuel. The water-gas is led from the bottom of the apparatus to the top, where it enters at the summit of the superheater, meets the oil, and passes down with it through the chamber, the finished gas escaping at the middle of the apparatus. This idea of making the air-blast pass up through the fuel, while in the subsequent operation the steam passes down through it, is also to be found in the Loomis plant, and is a distinct advantage—the fuel being at its hottest where the blast has entered; and, in order to keep down the percentage of carbon dioxide, it is important that the fuel through which the water-gas last passes should be as hot as possible to ensure its reduction to carbon monoxide.

The Flannery apparatus is also only a slight modification of the Lowe plant; the chief difference being that, as the water-gas leaves the generator the oil is fed into it, and with the gas passes through a Ω -shaped retort tube, arranged round three sides of the top of the generator. In this tube the oil is volatilised, and passes with the gas to the bottom of the superheater, in which the vapours are converted into permanent gases.

The Van-Steenbergh plant stands apart from all other forms of carburetted water-gas, in that the upper layer of the fuel itself forms the superheater, and that no second part of any kind is needed for the fixation of the hydrocarbons. This arrangement reduces the apparatus to the simplest form, and leaves no part of it which can choke or get out of order—an advantage which will not be underrated by anyone who has had experience of these plants. While, however, an enormous advantage is gained there is also the drawback that the apparatus is not at all fitted for use with crude oils of heavy specific gravity, such as can be dealt with in the big external superheaters of the Lowe class of water-gas plant, but requires to have the lighter oils used in it for carburetting purposes. This which appears at first sight to be a disadvantage, is not altogether one, as, in the first place, the lighter grade of oils, if judged by the amount of carburetting property they possess, are cheaper per candle power added to the gas than the crude oils; while their use entirely does away with the formation of pitch and carbon in the pipes and purifying apparatus—a factor of the greatest importance to the gas manufacturers. The fact that light oils give a higher carburation per gallon than heavy crude oils is due to the fact that the crude oils have to be heated to a higher temperature to convert them into permanent gases, and this causes an over-cracking of the most valuable illuminating constituents. This trouble cannot be avoided; as, if a lower temperature is employed, the result is the formation of non-permanent vapours, which, by their condensation in the pipes, give rise to endless trouble. The simplicity of the apparatus is a factor which is a considerable saving of time and expense, as it reduces to a minimum the risk of stoppages for repairs; while the initial cost of the apparatus is necessarily low, and the expense of keeping it in order practically nil.

In such an apparatus, 1000 cubic feet of carburetted water-gas having an illuminating value of 22 candles can be made with the consumption of about 30 lbs. of coke or anthracite, and 2.5 gallons of light naphtha.

The great objection to the use of carburetted water-gas

is undoubtedly the poisonous nature of the carbon monoxide, which acts by diffusing itself through the air-cells of the lungs, and forming with the colouring of the blood corpuscles a definite compound, which prevents them carrying on their normal function of taking up oxygen and distributing it throughout the body and at once stops life. All researches on this subject point to the fact that something less than 1 per cent only of carbon monoxide in air renders it fatal to animal life; and this, at first sight, seems to be an insuperable objection to the use of water-gas. It has, indeed, influenced the authorities in several towns—notably Paris—to forbid the introduction of water gas for domestic consumption. It would be well, however, to carefully examine the subject and see, by the aid of actual figures, what the risk amounts to compared with the risks of ordinary coal gas. Many experiments have been made with the view of determining the percentage of carbon monoxide in air which is fatal to human, or, rather, to animal life; the most reliable, as well as the latest, results being those obtained by Dr. Stevenson of Guy's Hospital, after an investigation instituted in consequence of two deaths which took place at the Leeds Forge, from inhaling uncarburetted water-gas containing 40 per cent of carbon monoxide. Dr. Stevenson found that 1 per cent visibly affected a mouse in $1\frac{1}{2}$ minutes, and killed it in an hour and three quarters; while 0.1 per cent was highly injurious. Taking, for the sake of argument, the last figure as being a fatal quantity, so as to be well within the mark, it is found that in ordinary carburetted water-gas, as supplied by the superheater processes such as the Lowe, Springer, and others, the usual amount of carbon monoxide is 26 per cent; but in the Van Steenberg gas, for certain chemical reasons to be discussed later on, it is generally about 18 per cent, and rarely rises to 20 per cent. An ordinary bedroom is 12 ft. by 15 ft., and 10 ft. high; and therefore it will contain 1800 cubic feet of air. Such a room would be lighted by a single ordinary batwing burner, consuming not more than 4 cubic feet of gas per hour, and if this were left full on, in one hour the 1800 cubic feet of air would be mixed with four-fifths of a cubic foot of carbon monoxide (the carburetted water-gas being supposed to contain 20 per cent), or 0.04 per cent. In such a room, however, if the doors and windows were absolutely air-tight and there were no fire-place, diffusion through the walls would change the entire air once in an hour. Therefore the percentage would not rise above 0.04, while in any ordinary room imperfect workmanship and an open chimney would change it four times in the hour, and reduce the percentage to 0.01—a quantity which the most inveterate enemy of water-gas could not claim would do more than produce a bad headache. The point under consideration, however, was the use of carburetted water-gas as an enricher of coal-gas, and not as an illuminant to be consumed *per se*; and it might be calculated that it would be probably used to enrich a 16-candle coal gas up to 17.5-candle power. To do this, 25 per cent of 22-candle power carburetted water gas would have to be mixed with it. Taking the quantity of carbon monoxide in London gas at 5 per cent (a very fair average figure), and 18 per cent as the amount present in the Van Steenberg gas, we have 8.25 per cent of carbon monoxide in the gas as sent out—a percentage hardly exceeding that which is found in the rich canal gas supplied to such places as Glasgow, where it is not found that an unusual number of deaths occur from carbon monoxide poisoning. Moreover, carburetted water gas has quite as strong a smell as coal gas, and can be quite as easily detected by the nose.

The cost of most of these methods of enriching coal gas can be calculated, and give the following figures as the cost of enriching a 16-candle gas up to 17.5-candle power per 1000 cubic feet:—

By canal coal	4d.
By the Maxim-Clark process .. .	2½d.
By the Lowe or Springer water gas ..	1½d.
By the Van Steenberg water gas ..	¾d.

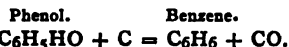
In adopting any new method, the mind of the gas manager must, to a great extent, be influenced by the circumstances of the times; and the enormous importance of the labour question is a main factor at the present moment. With masters and men living in a strained condition, which may at any moment break into open warfare, the adoption of such water-gas processes would relieve the manager of a burden which is growing almost too heavy to be borne. Combining, as such processes do, the maximum rate of production with the minimum amount of labour, they practically solve the labour question. The cost of paraffin oil of lighter grades, and the fear that the supply might be hampered by the formation of a huge monopoly, has been a great drawback; but we have materials which can be equally well used in this country, and of which an almost unlimited supply can be obtained.

At three or four of the Scotch iron-works, the Furnace Gases Company are paying a yearly rental for the right of collecting the smoke and gases from the blast-furnaces. These are passed through several miles of wrought-iron tubing, gradually diminishing in size from 6 feet to about 18 inches; and as the gases cool, there is deposited a considerable yield of oil. At Messrs. Dixon's, in Glasgow, which is the smallest of these installations, they pump and collect about 60 million feet of furnace gas per day, and recover, on an average, 25,000 gallons of furnace oils per week; using the residual gases, consisting chiefly of carbon monoxide, as fuel for distilling and other purposes, while a considerable yield of sulphate of ammonia is also obtained. In the same way a small percentage of the coke-ovens are fitted with condensing gear, and produce a considerable yield of oil, for which, however, there is but a very limited market; the chief use being for the Lucigen light and other lamps of the same description, and also for pickling timber for railway sleepers, &c. The result is that four years ago the oil could be obtained in any quantity at ¼d. per gallon, though it has since been as high as 2½d. a gallon. It is now about 2d. per gallon, and shows a falling tendency. Make a market for this product, and the supply will be practically unlimited, as every blast-furnace and coke-oven in the kingdom will put up plant for the recovery of the oil. As, with the limited plant now at work, it would be perfectly easy to obtain 4 or 5 million gallons per annum, an extension of the recovery process would mean a supply sufficiently large to meet all demands.

Many gas managers have from time to time tried if they could not use some of their creosote oil for producing gas; but on heating it in retorts, &c., they have found that the result has generally been a copious deposit of carbon, and a gas which has possessed little or no illuminating value. Now the furnace and coke-oven oils are in composition somewhat akin to the creosote oil; so that, at first sight it, does not seem a hopeful field for search after a good carburetter. But the furnace oils have several points in which they differ from the coal-tar products. In the first place, they contain a certain percentage of paraffin oil; and, in the next, do not contain much naphthalene, in which the coal-tar oil is especially rich, and which would be a distinct drawback to their use. The furnace oil, as condensed, contains about 30 to 50 per cent of water; and, in any case, this has to be removed by distilling. Mr. Staveley has patented a process by which the distillation is continued after the water has gone off; and, by condensing in a fractionating column of special construction, he is able to remove all the paraffin oil, a considerable quantity of cresol, a small quantity of phenol, and about 10 per cent. of pyridine bases—leaving the remainder of the oil in a better condition, and more valuable for pickling timber, its chief use.

If the mixed oil so obtained, which we may call "phenoloid oil," is cracked by itself, no very striking result is obtained; the 40 per cent of paraffin present cracking in the usual way, and yielding a certain amount of illuminants. But if the oil is cracked in the presence of carbon, and is made to pass over and through a body

of carbon heated to a dull red heat, it is converted largely into benzene. As this is the most valuable of the illuminants in coal gas, and also the one to which it owes the largest proportion of its light-giving power, it is manifestly the right one to use in order to enrich it. On cracking the phenoloid oil, the paraffin yields ethane, propane, and marsh gas, &c., in the usual way; while the phenol interacts with the carbon to form benzene:—



And in the same way the cresol first breaks down to toluene in the presence of the carbon; and this in turn is broken down by the heat to benzene. A great advantage this oil has is that the flashing-point is 110, and so is well above the limit; this doing away with the dangers and troubles inseparable from the storage of light naphthas in bulk.

In using this oil as an enricher, it must be cracked in the presence of carbon, and it is of the greatest importance that the temperature should not be too high, as the benzene is easily broken down to simpler hydrocarbon of far lower illuminating value.

THE ANALYSIS OF CUPRIC BROMIDE, AND THE ATOMIC WEIGHT OF COPPER.*

By THEODORE WILLIAM RICHARDS.

(Concluded from p. 36).

FOLLOWING are the essential data of all the experiments made with the pure solution of crystallised cupric bromide. The results are expressed in the same terms as those given above, and from the combination of these figures a final average value for the atomic weight of copper may be readily deduced.

FINAL ANALYSES.

Determination of Copper.

No. of experiment.	CuBr ₂ solution taken. Grms.	Copper found (reduced to vacuum). Grms.	Copper (red. to vac.) in 50 grms. solution. Grms.
18.	61.583	0.6744	0.54755
19.	51.955	0.5689	0.54750

Average 0.54753

Determination of Bromine.

No. of experiment.	CuBr ₂ solution taken. Grms.	Silver bromide found (reduced to vacuum). Grms.	Bromine (red. to vac.) in 50 grms. solution. Grms.
20.	25.998	1.68205	1.3767
21.	25.957	1.6789	1.3762
22.	25.935	1.6779	1.3766

Average 1.3765

Determination of Silver.

No. of expt.	CuBr ₂ solution taken. Grms.	Silver required (red. to vac.).		Silver (red. to vac.) for 50 grms. solution. Grms.
		Direct titration. Grms.	Sulpho-cyanide. Grms.	
23.	25.998	—	0.9664	1.8586
24.	25.957	0.9645	—	1.8579
25.	25.935	0.9640	0.9638	1.8583
Average				1.8583

* Contributions from the Chemical Laboratory of Harvard College. —From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxv.

Atomic Weight of Copper.

Calculated from the data given above, on the assumption that Ag : Br = 108.00 : 80.007.

			Atomic weight of copper. [Br=80.007.]
I.	From experiments 18 and 20		= 63.643
II.	" "	18 "	21 = 63.664
III.	" "	18 "	22 = 63.648
IV.	" "	19 "	20 = 63.636
V.	" "	19 "	21 = 63.657
VI.	" "	19 "	22 = 63.641

Average 63.648

VII.	From experiments 18 and 23		= 63.634
VIII.	" "	18 "	24 = 65.659
IX.	" "	18 "	25 = 63.645
X.	" "	19 "	23 = 93.628
XI.	" "	19 "	24 = 63.653
XII.	" "	19 "	25 = 63.638

Average 63.643

Total average = 63.645

Highest value = 63.664

Lowest " = 63.628

Greatest variation from mean = ± 0.018

If Ag = 108, result previously published = 63.640

" " accepted value (Hampe) = 63.37±

Each analytical result is combined with every other result above, in order that a better idea may be obtained of the variations of the figures. The combination of the averages of the three series of analyses would of course have given the same final average in a much more simple manner. Of the tabulated experiments, No. 23 is the least reliable, for the reasons before given; and rejecting values VII. and X. upon this ground, the total average would become 63.648, with a "probable error" of about ± 0.002.

The importance and value of the method of analysis, involving as it does the weighing of the silver used as well as of the argentic bromide formed, must be at once evident. Not only does the method give two wholly distinct classes of results for the atomic weight of copper, but besides this the relative weights of silver and bromine afford the sharpest possible test of the purity of the materials and the accuracy of the work. This method was first used by Professor Cooke in verifying the atomic weight of antimony, and he strongly insisted on the strength of the evidence thus furnished; although the point has been strangely overlooked by commentators.

Percentage of Silver in Argentic Bromide.

From experiments 20 and 23	= 57.454
" " 21 " 24	= 57.448
" " 22 " 25	= 57.447

Average = 57.450—

Average rejecting expt. 23 as before = 57.448—

According to Stas = 57.445

Previous determinations made in this Laboratory by various experimenters have given values ranging from 57.442 to 57.450

The agreement of the present value of the atomic weight of copper with the result which I previously published in the *Proceedings of the American Academy of Arts and Sciences*, vol. xxiii., p. 180, is a rather remarkable one, especially since the methods of work were wholly different in the two cases. The very slight difference between the preliminary and final results of this

* *Proceedings of the American Academy of Arts and Sciences*, xvii., 19; also Huntington on "Atomic Weight of Cadmium," *Ibid.* xvii., 28.

paper has already been explained, so that all the experiments which have been tried in this laboratory point to precisely the same figure.

In this connection it is worthy of notice that H. Baubigny,* a recent experimenter upon the atomic weight of copper, dried cupric sulphate at 440° without evidence of the formation of basic salt, and from the weight of copper oxide produced by the ignition of this salt obtained the value 63.47 for the constant under discussion. Baubigny's experiments are too briefly described to be fairly discussed, but their evidence agrees with that of the results of Shaw† in pointing toward a higher value of the atomic weight of copper than that usually accepted.

In the critical review of the present investigation it must be remembered that three distinct methods have been used, the last two being united for the sake of convenience. The chief probable constant error in the first series, given in the two preceding papers, is the chance of a secondary reaction between the copper and the argentic nitrate; but the purity of the silver produced, the absence of the slightest gas evolution during the progress of the chemical action, and the total lack of effect of dilution upon the final result, alike point to the conclusion that no such secondary action took place. In the research upon cupric bromide the chief probable constant error which could raise the observed atomic weight of copper is the presence of basic salt in the solution, but the final crystallisation of a neutral salt from an acid solution makes this chance very unlikely. Moreover, the basic salt was shown to be perfectly insoluble in water, and a direct experiment with methyl-orange proved the solution to be normal.

While no experimental knowledge can be said to be even relatively certain, and these with all other results are submitted only to be revised, and perhaps changed, by later experimentation, careful thought seems to show that the presumption is now upon the side of the later determinations of the atomic weight of copper.

During the last few years the atomic weights of antimony‡ and of cadmium§ have also been determined in this Laboratory, and have been referred to the same elements as those used in the present work. A statement of the final comparison might not be uninteresting.

Ag : Br : Sb : Cd : Cu = 108.00 : 80.00 +
+ : 120.00 : 112.31 : 63.64.

The collective results of the research must now be referred to the various different units of atomic weight usually adopted. Recently, an investigation|| has been conducted here upon the atomic weight of oxygen, and since then many other investigators¶ have taken up the same subject, all but one** confirming the result of that work. In view of this fact, and also in the light of the recent re-calculation of Stas's results,†† it seems not out of place to state the value of the atomic weight of copper upon the basis O = 15.87, as well as according to the usual standards.

Atomic Weight of Copper.

If Ag = 108.00	From [Cu : 2Ag]	Cu = 63.640
	From [CuBr ₂ : 2AgBr]	Cu = 63.648
	From [CuBr ₂ : 2Ag]	Cu = 63.643
Average		= 63.644

* *Compt. Rend.*, xcvi., 854, 906.

† *Phil. Mag.*, 3th Series, xxiii., 138.

‡ J. P. Cooke, *loc. cit.*

§ O. W. Huntington, *Proceedings American Academy*, xvii., 28.

¶ Cooke and Richards, *Proceedings American Academy*, xxiii., 149 and 182. Result, O = 15.87.

¶ Lord Rayleigh, *Roy. Soc. Proc.*, xliii., 356 (1888); W. A. Noyes, *Am. Chem. Journal*, xi., 155, xii., 441; E. W. Morley, results as yet unpublished. Also discussions by Crafts, *Compt. Rend.*, cvi., 1662, and many others.

** Keiser, *Am. Chem. Journal*, x., 249. Result, O = 15.95.

†† J. D. Van der Plaats, *CHEM. NEWS*, liv., 186. These results point to a value of oxygen between 15.87 and 15.89.

If Ag = 107.93	(O = 16.000)	Cu = 63.60
If Ag = 107.675	(Clarke)	Cu = 63.45
If Ag = 107.66	(Meyer and Seubert)	Cu = 63.44
If Ag = 107.06	(O = 15.87)	Cu = 63.09

In conclusion, the writer would express his deep sense of obligation to the kind friends whose interest and advice have so materially assisted the progress of the investigation.

SEPARATION OF BARYTA, STRONTIA, AND LIME.

By A. RUSSMANN.

(Concluded from p. 14.)

Method of E. Fleischer.

FOR the separation of barium, strontium, and calcium this method directs that the precipitated carbonates, after weighing, should be dissolved in a measured quantity of hydrochloric acid of known strength, the excess of acid titrated back, the barium precipitated with potassium chromate from the neutralised solution, the barium chromate being determined volumetrically with ferrous sulphate. The proportion of calcium and strontium is calculated from the amount of baryta found, and the quantity of hydrochloric acid consumed in dissolving the weighed carbonates after deducting the proportion belonging to the baryta.

Russmann has shown, in speaking of the method of Frerichs, under what conditions the determination of barium and its separation from strontium can best be effected. As for the volumetric determination of barium chromate with ferrous sulphate, it does not, according to Russmann, lead to satisfactory results. The washed precipitate was dissolved in hydrochloric acid, the barium thrown down with sulphuric acid, the filtrate titrated with ferrous sulphate, and the excess of the latter determined with permanganate. The results were always too low.

If only barium and calcium have to be determined in the absence of magnesia, Fleischer converts the barium into sulphate and the calcium into carbonate by digesting the solution of both with a mixture of 3 parts potassium sulphate and 1 part potassium carbonate. The precipitate is dried and ignited, and the calcium carbonate present is determined volumetrically.

According to the experiments of Russmann this method may be used successfully.

Method of W. G. Leison.

W. Gibbs has already shown that some metals may be determined by precipitating their sulphates, nitrates, or chlorides in a concentrated solution with oxalic acid and strong alcohol, and determining the oxalic acid in the precipitate by titration with permanganate. Alkaline salts must, of course, not be present.

Leison has applied this method to the determination of calcium, strontium, and barium. For the decomposition of the oxalates he uses either hot hydrochloric acid or ordinary dilute sulphuric acid. In the latter case the solution must be filtered through sand, as sulphuric acid dissolves matter out of paper filters, which is capable of acting upon permanganate. Barium oxalate cannot be completely decomposed by sulphuric acid, as the barium sulphate formed occludes undecomposed barium oxalate.

For the determination of calcium Russmann obtained good results with this method. He finds the use of paper filters admissible, even if the calcium oxalate is decomposed with sulphuric acid; but the titration must be effected in a very dilute solution to prevent a separation of calcium sulphate possibly accompanied by calcium oxalate.

Similarly satisfactory results were obtained on determining strontium oxalate. The sulphuric solution be-

comes, indeed, at once turbid, and a strong precipitate is formed on heating, but the strontium sulphate does not carry down any oxalate.

In determining barium, Russmann, like Leison, could not effect the complete decomposition of barium oxalate with sulphuric acid. If the precipitate was dissolved in hydrochloric acid, carefully avoiding excess, good results were obtained on titrating the highly diluted solution. In the majority of cases an ignition of the precipitates of the earthy oxalates is found more expeditious.—*Zeit. für Anal. Chemis.*

ON THE QUESTION OF CONCORDANCE IN ATOMIC WEIGHT DETERMINATIONS.

By F. W. CLARKE.

In the determination of atomic weights the subject of constant errors has of late years received much attention. On the experimental side, that is with reference to individual series of data, the possibility of constant error is always carefully considered; but another phase of the question, involving antecedent values, is too apt to be ignored. Under the latter heading one special case is familiar to all chemists, namely, the uncertainty in the ratio between oxygen and hydrogen, in consequence of which we have two distinct standards for atomic weights, the one $H = 1$, the other $O = 16$. The difference between these standards is small in itself, but among the higher atomic weights it becomes multiplied to serious proportions. In other words, if the atomic weight of hydrogen be taken as unity, the uncertainty in the atomic weight of oxygen becomes a large constant error in the calculation of other values. This particular error is merely a type of its class; for whenever an atomic weight is computed from other atomic weights which are assumed to be known, their errors, together with the experimental errors of the determinations themselves, are accumulated in the final result. Thus it sometimes happens, when an atomic weight has been determined by different methods, involving the use of different compounds, that the concordance or discordance between the several series of data obtained may depend upon the factors assumed in the final calculation. These factors are themselves subject to errors, great or small, which become constant errors in calculation, and which, although cumulative in their effects, are commonly neglected altogether. Only those determinations of atomic weight which depend upon direct comparison of an element with the standard of value are free from errors of this class.

In a recent paper upon the atomic weight of cadmium, by E. A. Partridge,* the foregoing suggestions are well exemplified. Experimentally Mr. Partridge's work appears to be excellent, and on their face his results are concordant in the highest degree. Three methods were adopted for the determinations as follows:—First, the ignition of CdC_2O_4 to CdO ; second, the conversion of $CdSO_4$ into CdS by heating in a stream of H_2S ; third, a similar conversion of CdC_2O_4 into CdS . In each series ten experiments were made, and from each experiment individually the atomic weight of cadmium was computed. In brief, the results obtained were as follows, omitting details and taking $O = 16$ as the standard of comparison:—

	$CdC_2O_4 : CdO.$	$CdSO_4 : CdS.$	$CdC_2O_4 : CdS.$
Cd = maximum,	111.834	111.818	111.833
minimum,	111.759	111.778	111.771
mean,	111.8027	111.7969	111.805

The mean of all is $Cd = 111.8015$, with an extreme range from lowest to highest of only 0.075.

Curiously, however, Mr. Partridge does not state what values he assumed for the atomic weights of carbon and sulphur in making his computations. Working back from some of his figures, I find that he must have taken the round numbers 12 and 32; and just here the question of concordance may be raised. In a re-calculation of the data I have reduced all the experiments to percentage form, getting the averages of the three series into the subjoined proportions:—

1st series, $CdC_2O_4 : CdO :: 100 : 63.964$	± 0.0011 .
2nd series, $CdSO_4 : CdS :: 100 : 69.199$	± 0.0012 .
3rd series, $CdC_2O_4 : CdS :: 100 : 71.973$	± 0.0007 .

Now, when $O = 16$, these ratios give equations containing each an absolute term. If we compute with $C = 12$ and $S = 32$, we get one set of values for Cd ; if we take Stas' figures, $C = 12.005$ and $S = 32.074$, we get another set; and if we assume the factors given in my own "Re-calculation of the Atomic Weights," viz., $C = 12.001$ and $S = 32.058$, we have still a third series. The results are as follows, in mean:—

	C, 12. S, 32.	C, 12.001. S, 32.058.	C, 12.005. S, 32.074.
1st series, Cd = 111.801		111.8036	111.8178
2nd series, Cd = 111.785		111.7271	111.7111
3rd series, Cd = 111.808		111.6054	111.5788
Range,	.023	.1082	.2390

Hence we see clearly that the concordance between the three series of determinations is conditioned, under the ordinary modes of calculation, by the uncertainties in the factors used. If the concordance shown by Partridge is real, Stas' values for C , or S , or both, are in error. If Stas' values are correct, then the three series of Mr. Partridge are discordant by nearly one-fourth of a unit in the atomic weight of cadmium. The small variations in the low atomic weights are multiplied in the higher figures.

In a discussion of this sort it is perhaps not possible to establish any distinct criterion of accuracy by means of which constant errors can be detected and placed. It is possible, however, at least in certain cases, to so handle data that the results of calculation shall involve no extraneous uncertainties. In the present instance the ratios measured by Partridge are capable of quite independent discussion, and by the simplest of means.

If we continue to put $O = 16$ as our standard of comparison, and use the symbols of the elements algebraically to represent atomic weights, the three proportions given above may be transformed into the following linear equations:—

1st series, $36.036Cd = 127.928C + 2493.696$.
2nd series, $30.801Cd = -30.801S + 4428.736$.
3rd series, $28.027Cd = 143.946C - 100S + 4606.272$.

Here we have three equations with three unknown quantities, Cd , C , and S , and no assumption need be made in advance as to the value of either. Solving directly, these equations give us the following results:—

$$\begin{aligned} Cd &= 111.7850 \\ C &= 11.9958 \\ S &= 32.0002. \end{aligned}$$

These values are independent of all other determinations, and contain only the errors of Partridge's own work, divided into three portions, instead of being accumulated upon the atomic weight of cadmium alone. They involve, however, the assumption that the three sets of observations are of equal weight, which may or may not be true. If different weights are assigned we must then form normal equations by the method of least squares, and their solution might modify our final figures. For present purposes, however, the more laborious method of computation, with its discussion of weights and probable errors, is quite unnecessary. Such a discussion may be found in Strecker's re-calculation of Liebig and Redtenbacher's

data relative to the atomic weight of carbon.* So far as I know, that paper stands alone in chemical literature, the only one of its kind.

Recurring now to the three atomic weights deduced from the three equations, we find that the values for carbon and sulphur vary slightly from the best recognised determinations. The extent of that variation may perhaps serve as an index of the accuracy of the work done, and the question of concordance of data assumes a new form. The more nearly the figures for C and S agree with established values, the better the determinations probably are; and in the present case the agreement is close enough to establish a reasonable presumption in favour of Partridge's methods. The constant errors in his work cannot be large, and they are probably all in one direction.

But between Partridge's determinations, however discussed, and the atomic weight of cadmium as measured by either Dumas or Huntington, there is a discordance of nearly half a unit. The latter chemists, both working with haloid salts of cadmium, are in close agreement; and their data, with Stas' values for Ag, Cl, and Br, and with O = 16, make Cd about 112.23, very nearly. This discordance is probably real, and due mainly to differences in experimental methods. Its cause can only be found by further experiments, and certain lines of investigation are easily suggested. Apart from the obvious plan of scrutinising each method by itself, and seeking for the constant errors which must exist on one side or the other, it is clear that new modes of determination should be attempted, lying between and connecting the existing data. For example, the ratios $CdO : CdSO_4$, $Cd : O$, $Cd : S$, $Cd : Ag$, $Cd : Cl$, and $Cd : Br$ are all apparently capable of direct measurement; and they would, if determined, serve to check each other and to control the older determinations. A system of such interlacing ratios can be discussed collectively, by least squares, so as to distribute errors of observation, the constant error of any one series of data being equivalent to an accidental error in its relations to the other series. In a large system of ratios the constant errors can hardly be all in one direction, and they must tend to neutralise each other to a very considerable degree. Each ratio should contribute to our knowledge of every atomic weight involved in it, and not be considered solely with reference to a single component. The current methods of computation are fallacious in so far as they tend to magnify and accumulate errors which could be partially eliminated.—*American Chemical Journal*, vol. xiii., No. 1.

A CURIOUS FORMATION OF THE ELEMENT SILICON.

By H. N. WARREN, Research Analyst.

DURING the preparation of specimens of crystalline and other forms of silicon, I obtained a most curious formation of that substance, which would appear, when tested analytically, to be composed of graphitoid silicon, constituted so as to form most perfect and well-developed crystals consisting of oblique octahedrons. This peculiar form of silicon first made its appearance upon subjecting potassium silicofluoride to a most intense heat in contact with impure aluminium. Upon separating the graphitoid silicon thus formed by the aid of dilute acids, small quantities of the other substance was observed. Direct steps were at once taken to procure it, if possible, in larger quantities, after numerous experiments had failed to reproduce it; the following method was used with success, although still very uncertain. Graphitoid silicon was first obtained by introducing pieces of metallic aluminium about the size of a walnut into a

clay crucible of convenient dimension, and subjected to a heat sufficient to maintain in a fused state a mixture of four parts potassium silicofluoride, one of potassium carbonate, and two of potassium chloride. After the violent reaction attending the introduction of the aluminium had subsided, the crucible was urged to whiteness for about five minutes; after cooling and breaking the same a perfect round button containing about 80 per cent of silicon was obtained. This, after carefully detaching any adhering slag, was placed in a plumbago crucible containing about twelve times as much aluminium as the button obtained, together with an addition of two parts of metallic tin, and covered with a layer of sodium silicate. The crucible and its contents were then subjected to the most powerful heat that could be obtained for about two hours; after cooling the same and breaking the piece of aluminium contained therein, the new modification was obtained in large perfect crystals possessing a full metallic lustre and true models of oblique octahedrons. After dissolving the small quantity of aluminium mechanically entangled, the analysis of the residue showed pure silicon, insoluble in all acids except hydrofluoric and infusible. In appearance the crystals resemble crystals of cast-iron which are sometimes met with upon breaking a pig of that substance, the largest assuming a size of over half an inch across the faces, and as perfect as a crystal of alum.

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THE FILTRATION OF NATURAL WATERS.*

By THOMAS M. DROWN,
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IN the study of the subject of filtration of water for drinking purposes, we shall arrive at no clear and valuable ideas unless we distinguish sharply between mechanical filtration, which deals only with the interception and retention in the filter of the solid particles suspended in the water, and filtration combined with the oxidation of organic matter, — that in solution, as well as that in suspension in the water. This latter process — the purification of the water by the oxidation of its organic contents — can be accomplished only by *intermittent* filtration; the former — the mere removal of the solid particles in the water — may be accomplished by *continuous* filtration, as practised in many large cities in Europe.

When we speak of the purification of water by filtration, we mean in a general way, that a water is thereby rendered fit to drink which was unfit or unattractive before it was filtered. The change effected by filtration may be simply the removal of vegetable or earthy matters, whereby the water is made more palatable and more attractive in appearance, or it may be more radical, in converting water which was positively harmful into a good drinking water. Widely different in action as are the two systems of filtration, the intermittent and the continuous, yet it is possible by both systems to improve the quality of a bad water.

In the system of continuous filtration, in which there is little or no change made in the dissolved organic matter, it might at first thought seem as if there could be only imperfect purification; but it must be borne in mind that it is possible in this system to remove in great part even those very minute organisms, the bacteria.

The germ theory of disease furnishes us with the simplest explanation of the way in which water does harm, and if we can, by simple mechanical filtration, remove the harmful germs from the water, we have effected a true and efficient purification of that water, whatever

* *Ann. Chem.* (Liebig) lix., 280 (1846).

* From a Paper read January 15, 1890. Reprinted in part from the *Journal of the Association of Engineering Societies*.

may be its chemical composition. Let us push this idea a little further. If we take as the basis of our theory of harmfulness of water that disease is caused by it only when micro-organisms are present in it, then, if we could by the continuous filtration of sewage remove absolutely all the germs which it contained, leaving unchanged its other characters—appearance, taste, odour, &c.—this sewage would be perfectly safe to drink. To put the matter in another form, a sterilised water or sewage has no possibilities of producing disease except so far as it may contain saline or other substances which may produce derangements of the system, in the same way as would a drug—a dose of salts or of senna. It is foreign to my present purpose to consider whether our knowledge at present justifies this position, but it is important to bear it in mind in judging of the efficiency of filtration.

When water is said to be well, or moderately well, or completely purified by filtration, we cannot know what is meant unless we know what is the standard of purity implied. Is it simply the removal of colour, odour, and suspended matter; is it chemical purity, meaning thereby the absence of unoxidised organic matter, or is it bacterial purity, or freedom from germs? Again, what shall we say of water of high chemical purity, with high bacterial contents; or what of a water with few or no bacteria which contains considerable organic matter capable of undergoing change?

Intermittent filtration is capable of giving water free from organic matter and free from germs; continuous filtration, if conducted very slowly, is capable of giving water free from bacteria, without odour and colour, but which may contain much dissolved organic matter. Intermittent filtration effects the oxidation of the organic matter in solution as well as that in suspension; continuous filtration has little or no effect on the organic matter in solution.

After laying such stress on the removal from water of bacteria, it sounds like a paradox to say that purification both by intermittent and continuous filtration depends on the presence in the filter of bacteria in enormous numbers, and that without them the purification would, in both cases, be impossible.

The idea is not a new one that the bacteria of decomposition are benign and useful organisms which break up organic matter, rearrange its atoms, and convert it into mineral matter, so that it may again serve as food for plants. If we keep away the bacteria from a mass of dead organic matter it undergoes no change whatever. All processes of decay of organic matter are absolutely dependent on the presence of these micro-organisms, which, so far as we know, have no other than a beneficial *role* to play in nature. I say this is now a matter of common knowledge, and one is therefore not unprepared to hear, that in the purification of water by intermittent filtration the ground or sand upon which the water is poured is full of bacteria; in fact, that it is the design of the process to cultivate them and have as many of the micro-organisms in a cubic inch of ground as possible.

If one pours over a column of clean, bright sand, free from bacteria, impure water, as sewage, it will flow out about as bad as it entered the sand. But if it is poured over a column of sand in which septic bacteria have been cultivated, so that the sand may be said to be fairly reeking with bacteria by the million, the water may flow out as pure (organically) as spring water. But even in continuous filtration, where there is little or no oxidation going on, the bacteria are, according to Piefke (the engineer of the Berlin water-works), the efficient agents in removing the suspended matters, including the micro-organisms in the water. To this subject we will return later; let us first briefly study the nature of oxidising or intermittent filtration on the typical polluted water, namely sewage.

Sewage is a substance which contains all of its nitrogen in the unoxidised form. Its principal ingredient is free ammonia; it also contains considerable (but a much less

amount usually) organic nitrogen, or albumenoid ammonia, but of nitrous or nitric acid it contains none. When sewage is exposed to the air in mass, oxidation goes on very slowly, because it can only get air from its surface; when it flows out into streams, the oxygen dissolved in the water of the streams quickly oxidises the ammonia, and we find in the water a short distance below the entrance of the sewage nitrites and nitrates abundantly. When the sewage is exposed to the air in very thin layers, as when a porous material like sand is moistened with it, oxidation goes on with great rapidity. It was until recently considered that this oxidation was a direct chemical combination of the elements of the organic matter with the oxygen of the air, or the oxygen dissolved in the water, but we now know that nitrogen is not oxidised by the direct contact of decomposing nitrogenous matters with air unless bacteria are present, and the inference seems a fair one that the greater the number of bacteria the more rapid the process of oxidation. Sewage itself usually contains hundreds of thousands of bacteria to the c.c., which are dormant until air gets access to it. If sewage is preserved out of contact of air, the bacteria of decomposition will in time all die.

The experiments of the Massachusetts State Board of Health on the purification of sewage by intermittent filtration which have been carried on at Lawrence for the past two years, under the direction of Mr. Hiram F. Mills, the engineer member of the Board, have added largely to our knowledge of the conditions governing the purification of nitrogenous organic matter. Here are large tanks, one two-hundredth of an acre in surface, filled with different materials—coarse sand, fine sand, river silt, muck, garden soil, clay, &c., to the depth of five feet, on which is poured, from day to day, sewage in known amount and of known composition. The effluent water from this sewage filtration is collected, measured, and analysed, and the precise amount of purification determined. The result of two years' work at this station will shortly be published in the Report of the Board now in the press. I will at present give one or two of the facts that have been there developed. The purification of the sewage means the complete oxidation of all its organic ingredients both in solution and in suspension, the carbon to carbonic acid, the hydrogen to water, and the nitrogen to nitric acid. The filtering materials best adapted to the purpose are those which are fine enough to retain considerable sewage in their pores, and also plenty of air at the same time.

The body of porous material is, when in good working order, a very delicate machine. It must be coaxed up to its high efficiency by gradually increasing the amount of sewage. This means, in all probability, that we must develop in the pores of the sand an immense number of bacteria to be constantly on hand in the different layers to attend to the sewage as it reaches them. During the first winter there was no nitrification in these tanks, and consequently no perfect purification, but on the advent of spring, when the temperature of the effluent water reached 39° F. nitrification began and has continued ever since, the cold weather of the second winter failing to stop it.

The tank which has given the best results, that is, a good purification of the largest quantity of sewage for a long period, is filled with coarse mortar sand, most of the grains of which average about 0.06 in diameter. This has given an effluent day after day organically as pure as many drinking waters, when receiving sewage at the rate of nearly 60,000 gallons per acre per day.

One would naturally ask why is not this the ideal system of purification of all surface waters, even those that are not polluted by drainage of any kind, but which contain much vegetable suspended matter, and have, in consequence, sometimes a bad odour; or waters which are unattractive in appearance by reason of dissolved colouring matter?

One of the tanks of the Lawrence Experiment Station has filtered Merrimack water intermittently for more than

two years at the rate of 300,000 gallons per acre per day. The filtering material consists of 3' 8" of coarse and fine sand and fine gravel; 10" of yellow sandy loam, and 6" of brown soil in the same position as found on the river bank. During the day the surface of the sand is generally covered with a few inches of water, but at night and on Sunday air gets access to the sand. The following figures give the composition of the filtered water during last December, compared with the Merrimack water applied:—

	Merrimack River Water. Parts per 100,000.	Filtered Water. Parts per 100,000.
Turbidity	Very slight	None.
Sediment	"	"
Colour	0'35	0'0
Odour	Faintly vegetable	"
Total solids	4'2	3'5
Loss on ignition ..	1'6	0'9
Free ammonia	0'0015	0'0005
Albumenoid ammonia	0'0127	0'0059
Chlorine	0'18	0'18
Nitrogen as nitrates .	0'0124	0'0191
" " nitrites ..	None.	None.

The water is free from microscopic organisms, and the bacteria rarely exceed 10 or 20 per c.c., while the water applied has generally a few hundred. During the two years that this tank has been in operation the surface has not been cleaned or disturbed in any way. The slow rate of filtration (being only about one-half an inch an hour per square foot of surface), is due to the considerable amount of very fine material contained in the soil and loam.

But one must bear in mind, in connection with the rate of filtration, that the thoroughness of the purification, meaning thereby the oxidation of the organic matter, is much greater in intermittent than in continuous filtration.

This system of intermittent filtration for natural waters has never, I believe, been carried out on the large scale, although the possibility of its being practicable in some localities has been discussed. It is the system that nature suggests, for it is intermittent filtration which supplies the springs, which furnish the ideally pure and perfect drinking water. In the report of the Massachusetts State Board of Health to the Springfield Water Board with regard to the purification of the water of its Ludlow reservoir, which contains an immense growth of blue-green algae, Mr. Stearns, the chief engineer of the Board, suggested that surveys be made to discover, if possible, suitable ground conveniently situated, on which to pour intermittently the water of the reservoir, and to collect it again at lower levels in wells and springs. It is probable that continuous filtration would be inapplicable to water of this kind, for the jelly-like masses which are secreted by these algae would probably close the pores of the filter in a very short time. With intermittent filtration the deposit of organic matters in the pores of the sand would dry out or become oxidised when the ground was more or less dry.

It has been to many a difficult matter to explain how filters working continuously, and constantly covered with water, could intercept objects so much smaller than the spaces between the particles of sand. It was easy to imagine that some of the minute suspended particles might be caught between the particles of sand, but that practically all the suspended matter, even the minute bacteria, could be removed in a good-working filter, seemed to indicate that the efficient working of a filter depended on the fact that it became nearly clogged on the surface by the algae and other matter which held back even the smallest objects. But if this were the case it would save time to use a finer sand at the outset which experiment shows will not accomplish the purpose.

Piefke* has given us the clearest conception of the

action of sand filters in removing the suspended matters, including bacteria, from surface waters. The chemical effect is very slight, as might be supposed when one reflects that the duration of the passage of the water through the sand seldom, if ever, exceeds five and a half hours, and since the filter is kept constantly covered, there is no oxygen present but that dissolved in the water. But the mechanical effect in removing suspended matter, mineral and organic, is very great. The Spree water, which forms part of the supply of Berlin, contains as high as 100,000 bacteria per c.c. at times, and the number in the filtered water rarely exceeds 100, that is, the reduction of bacteria may reach 99'9 per cent. The thickness of the sand layer is generally from 2' to 3', and this rests on a layer of coarser gravel which is without any effect on the filtration. The size of the sand is seldom finer than one-fiftieth of an inch, which leaves channels between the grains that 500 micro-organisms could pass abreast. Smaller still are the particles of clay which give a milkiness to water; and yet when one of these sand filters is working well, both clay and bacteria are held back in the sand.

It takes a new filter about two weeks to get to its maximum efficiency, and if the sand be first carefully cleaned and sterilised by heat, then it takes much longer, many weeks, before the filter works well.

On examining with the microscope the surfaces of the particles of sand when the filter is in perfect working order, they are found to be coated with a greasy, slimy substance which is a mass of bacteria jelly. Piefke found in a kilogram of sand taken from the surface of a filter 5,600,000,000 bacteria; just below the surface 734,000,000, and at the depth of a foot 92,000,000. These numbers, he says, are far below the truth, because of the difficulty of cleaning the particles of sand thoroughly. It is to this coating of bacteria jelly that Piefke attributes the efficiency of these filters, and until the jelly forms in sufficient amount to completely envelope each particle of sand, the filters work imperfectly. This, then, is his explanation of the fact that minute micro-organisms and particles of clay of infinitely smaller size than the channels in the sand are stopped in their passage through it—they are simply caught in this slimy coating and cannot get further.

A filter of this kind is, like that used in intermittent filtration, a very delicate instrument, and it is very easy to disarrange it. Disturbance of the sand or suddenly increasing the pressure of the water may have, as a consequence, a rush of bacteria into the filtered water. Quite regular working is an essential condition of success. The rate of filtration is on an average only four inches vertically an hour, so that in the passage of the water through the sand, one-third of which is interstitial space, its rate is three times as great, or twelve inches an hour, and the sand layer, being two feet thick, the water is in contact with the sand only two hours. In very turbid waters, or waters very high in bacteria, the filtration is often decreased to one-half this rate, or even less, and in comparatively clear water, with low bacteria, the rate may be doubled. The working of the filters in Berlin is governed entirely by the number of the bacteria in the filtered water, this being the simplest way of judging of the efficiency of their working. One hundred bacteria per cubic centimetre in the filtered water is considered a good result on the Spree water, which contains always many thousands. To give practically sterile water would require a diminished rate say to one vertical inch an hour, which would be impracticable without enlarging the filtering plant.

(To be continued.)

* Die Principien der Reinwasser Gewinnung vermittelst Filtration," p. 50, Berlin, 1887.

" Aphorismen über Wasserversorgung von hygienisch-technischen Standpunkte aus bearbeitet."—*Zeitschrift für Hygiene*, 1889, Vol. 7, p. 115.

With C. Frankel.—Ueber die Wirksamkeit der Sandfiltration zur Befreiung des Trinkwassers von etwaigen Infektionskeimen.—*Zeitschrift für Hygiene*, 1890, I.

* "Mittheilungen über natürliche und künstliche Sandfiltration," pp. 75, Berlin, 1887.

"Die Boden Filtration," p. 51, Berlin, 1883.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

January 16, 1891.

Prof. W. E. AYRTON, F.R.S., President, in the chair.

THE thanks of the meeting were unanimously accorded to the Maxwell Memorial Committee for presenting to the Society a copy of Maxwell's Scientific Papers.

Prof. G. M. MINCHIN, M. A., read a paper on "*Photo-Electricity*."

His experiments on the subject were commenced in 1877, in attempting to produce a photographic image of a distant object. The result sought for has not hitherto been obtained, but the experiments have led to the discovery of many interesting phenomena. Some of these were shown to the meeting.

Electric currents are produced by the action of light on silver plates coated with collodion or gelatin emulsions of bromide, chloride, iodide, and other silver salts, or with eosine, fluoresceine, and other aniline dyes, when the plates are immersed in a suitable liquid, and one plate is illuminated whilst the other is screened. The direction of the currents depend on the materials employed, and the blue end of the spectrum is most effective. Currents have a photographic effect on the plates, and this action is strictly confined to the parts through which the current has passed.

Comparatively strong currents are obtained from plates coated with eosine and gelatin. A curious reversal was observed with some cells, the exposed plate first being positive to the screened one, and almost immediately afterwards became negative. On shutting off the light, a transient increase of current resulted, and afterwards disappeared gradually.

M. Becquerel, who has studied the action of silver plates coated with bromide, &c., concludes that the nature of the exposed plate (whether positive or negative) depends on the thickness of the surface layer. The electromotive force of such cells rarely exceeds one-twentieth of a volt.

Uncleaned tin-foil plates in common tap water give a current when one is exposed to light and the other screened. Cleaning the plates destroys the effect. In nearly every case the exposed plate was first positive and after a time became negative; and by exposing various parts of a plate (some portions of which had been previously exposed) the currents could be varied in direction at will. These peculiarities may explain the known divergence of tin from Volta's law. The phenomena have also been studied by aid of the electrometer. Tin foil obtained from tobacco packages was found to be very sensitive to light. One side of such foil is dull and the other bright. By pasting slips of it on opposite sides of a glass plate so that dissimilar sides are outermost, and immersing them in alcohol, a cell giving an E.M.F. of $\frac{1}{25}$ th volt when the dull side was exposed to light was obtained. The addition of any salt to the liquid, with a view to diminishing the resistance, invariably reduced the E.M.F. Experiment showed that the alcohols were by far the best liquids to use with tin plates.

A process for producing very sensitive tin plates was described, which apparently results in the formation of white oxide of tin on the surface of the foil. With one such plate and another sensitised plate the best results have been obtained by immersing them in methyl alcohol prepared from oil of wintergreen. From experiments on the variation of E.M.F. with intensity of light, it was found that the square of the E.M.F. is proportional to the intensity.

Some tin cells behave in a very peculiar manner, for it often happens that a good cell will exhibit no E.M.F. after being kept a few days. A slight impulse or tap

given to the cell or its support restores the sensitiveness; another impulse makes the cell insensitive; and these effects can be repeated indefinitely. Such cells the author calls "impulsion cells," and some were exhibited at the meeting. The sensitised plate of one of these cells had different properties at its two ends, for impulses had no effect on the nature of the lower end, but changed the upper end from positive to negative and *vice versa*. Electro-magnetic impulses, such as produced by sparks, are capable of altering cells from the insensitive to the sensitive state, but fail to produce the reverse effect. A Hertz oscillator restored the sensitive state in a cell placed at a distance of 81 feet away. The "impulsion effects" can be got rid of by renewing the alcohol on several successive days.

During last year, the author made some selenium cells by spreading the melted substance on metal plates and immersing them in liquids together with an uncoated plate. Of the various metals and liquids tried, aluminium and acetone gave the best effects. The process of forming these "seleno-aluminium cells" was described. One of their peculiarities is that they are nearly equally sensitive to rays of all colours, and when exposed to strong light may give an E.M.F. of $\frac{1}{2}$ to $\frac{3}{4}$ of a volt, the sensitised plate being negative. An arrangement of 50 cells in series, with an electrometer, was exhibited, whereby the E.M.F. generated by light falling on the cells could be caused to ring a bell, light or extinguish electric lamps, &c.

In conclusion, the author pointed out the possible application of photo-electricity to photometry, telephotography, and the utilisation of solar energy.

At the request of the President, Prof. Minchin promised to show the experiments on February 13th, on which date the discussion on the paper is to take place.

Prof. F. R. BARRELL, B.A., exhibited and described "*A Lecture Room Apparatus for Determining the Acceleration due to Gravity*."

A number of iron balls are allowed to fall through a certain height in such a way that one starts off when its predecessor has arrived at its destination. From the time occupied by all the balls, the time for one can be found, and, knowing the distance traversed, "g," can be determined.

The apparatus consists of two electro-magnets, joined in series with a battery and key, together with a ball-feeding device. One of the magnets is vertically over the key, and serves to catch the balls as they emerge from the feeding tube, whilst the other magnet actuates a kind of slide for supplying successive balls.

When one ball falls on the key it breaks circuit, and thus causes the first mentioned magnet to let go its ball. The key then springs up again, thus making circuit, and the feeding magnet then supplies another ball, which is caught by the holding magnet until the falling ball reaches the key, and the operations are repeated. Fairly accurate results can be obtained by the apparatus.

Sir John Conroy's paper, "On the Change in the Absorption Spectrum of Cobalt Glass by Heat," was postponed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxii., No. 1, January 5, 1890.

On the Explosive Wave, on the Characteristic Data of Detonation and its Speed of Propagation in Solids and Liquids, and especially in Methyl Nitrate.—M. Berthelot.—The explosive wave with its

simple characters and its definite laws exist only in the detonation of gases. These laws and characters exist only in part in the detonation of liquids and solids.

On the Absorption-Spectra of Solutions of Iodine.—H. Rigollet.—Among homologous bodies or compounds of one and the same radicle used as solvents for iodine, it is found that as the molecular weight increases, the absorption band advances very slightly towards the violet end of the spectrum, whilst the minimum of light transmitted diminishes.

Influence of the Co-Volume of Gases upon the Speed of Propagation of Explosive Phenomena.—M. Vieille.—The speed of propagation of a very small shock, like the speed of sound in a very hot liquid, increases very rapidly with the gaseous condensation.

On the Conductivities of Isomeric Organic Acids and of their Salts.—D. Berthelot.—This paper is not adapted for useful abstraction.

On Triethenyl.—Adolphe Rénard.—Triethenyl forms yellow needles, which melt at 147° to a yellow liquid. It boils at 357°. It is very soluble in benzene, ether, chloroform, less soluble in alcohol, acetic acid, and petroleum essence. Its vapour density is 8.6, or theoretically 8.68.

Action of Sodium Benzylate upon Camphor Cyanide.—J. Minguin.—The author obtains a solid body which crystallises in fine transparent laminæ, melting at 70–71°. It dissolves readily in benzene, toluene, and xylene, even in the cold. It is less soluble in ether and in the methylic ethylic and propylic alcohols. Its rotatory power is $\alpha_D = +428^\circ$; its composition is— $C_{18}H_{23}O_2N$.

A General Method of Analysis of the Spirits and Alcohols of Commerce.—Ed. Mohler.—This paper will be inserted in full.

Revue Générale des Sciences Pures et Appliquées.
Vol. i., No. 23.

Recent Researches on Starch and the Diastases.—B. Petit.—The author recognises on the one hand the intervention of a diastase in the migration of starch from the leaves of plants to their seeds, and on the other hand the mode of action of the diastase and the composition of the extract of malt. But the constitution of starch is still unknown, and both the composition and the origin of the diastases have not been ascertained.

Journal de Pharmacie et de Chimie.
Vol. xxii., No. 2.

On the Densimetric Determination of Alcohol in Wines on the Principle of Tabarié.—Léon Perier.—The author deduces the alcoholic strength of wines from the difference between the specific gravity of the wine in its natural state, and when the alcohol has been expelled. His results are given in a table.

Colorimetric Method for Determining Tannin in Barks.—S. J. Hinsdale (*Amer. Jour. of Pharmacy*).—The author first prepares a ferric liquor by dissolving 0.04 grm. potassium ferricyanide in $\frac{1}{4}$ litre of water, and adding $\frac{1}{4}$ c.c. solution of ferric chloride. A tannic solution is then made by dissolving the same weight of pure tannin in an equal vol. of water. The substance in which it is intended to determine the tannin (oak-bark, galls, sumacs, catechu, &c.), is brought in contact with a little boiling water, and the solution is then diluted with cold water. For substances containing less than 10 per cent of tannin he operates upon 0.8 grm., and makes $\frac{1}{4}$ litre of solution; if from 10 to 20 per cent it is diluted 1 litre. On the contrary, if there is less than 1.5 per cent he operates with 8 grms. instead of 0.8 grm. Six flat-bottomed glasses are set upon white paper, and in the first there are put 5 drops of the solution to be titrated; into the others there are put, respectively, 4, 5, 6, 7, and 8 drops of the solution

of tannin. To each there are then added 5 c.c. of the ferric liquor, and after the lapse of three minutes he observes the tint of the tannin solution which corresponds the most closely with the solution under examination.

Vol. xxii., No. 3.

On Tetrachlorophenol.—Louis Hugouneq.—This compound has been obtained by saponifying anisol tetrachloride by hydriodic acid of specific gravity 1.7. The tetrachloro-anisol is heated for twenty hours in a closed vessel to 145°–148°, with four times its weight of acid. The composition of the product obtained is $C_6HCl_4.OH$. It is produced in white needles, which when pure melt at 152°. The new compound is insoluble in water, but soluble in all organic solvents, and boils at 278°. The alcoholic solution behaves like an acid with indicators, and it decomposes carbonates. It is not poisonous.

The Odoriferous Principle of the Seeds of Rosa Canina.—This odour is found to be actually due to the presence of vanillin in the seeds to the extent of 0.1 part per 1000. Vanillin has also been recognised in the seeds of the white lupin.—*Journal de Pharm. von Elsass Lothringen.*

MEETINGS FOR THE WEEK.

- MONDAY, 26th.**—Medical, 8.30.
Society of Arts, 8. "The Construction and Capabilities of Musical Instruments," by A. J. Hipkins, F.S.A.
- TUESDAY, 27th.**—Institute of Civil Engineers, 8.
Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley, F.R.S., B.S., F.R.C.S., Fullerian Professor of Physiology, R.I.
Royal Medical and Chirurgical, 8.30.
Society of Arts, 8. "Lithography: A Finished Chapter of Illustrative Art," by William Simpson.
- WEDNESDAY, 28th.**—Society of Arts, 8. "Illustrated Journalism," by Carmichael Thomas.
- THURSDAY, 29th.**—Royal, 4.30.
Royal Institution, 3. "The Little Manx Nation," by Hall Cairne.
- FRIDAY, 30th.**—Royal Institution, 9. "British Mosses," by The Right Hon. Sir Edward Fry, Lord Justice, F.R.S., F.S.A., F.L.S.
- SATURDAY, 31st.**—Royal Institution, 3. "Pre-Greek Schools of Art," by W. Martin Conway, M.A., F.S.A.

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THE CHEMICAL NEWS.

VOL. LXIII. No. 1627.

THE TELLURIC SCREW.

MANY of our readers will have felt surprised by the recent announcement that MM. Lecoq de Boisbaudran and A. de Lapparent have discovered a new claimant for priority in the recognition of the Periodic Law. Their surprise will not be lessened when they see the memoir which was read on the 12th instant, and which we reproduce textually. The chemist who is said to have anticipated Mr. J. Newlands, and *a fortiori* Professor Mendeleeff and Professor Lothar Meyer, in announcing the periodic arrangement of the simple bodies is M. Béguyer de Chancourtois. His researches, made known in 1862, have not been disinterested from some forgotten "*pli cacheté*," or found in the back numbers of some obscure journal. They are to be seen in the *Comptes Rendus*! Hence, MM. de Boisbaudran and Lapparent seek to know how these documents can have escaped the attention of Mr. Newlands? To answer one question by another we must ask how they can have escaped the notice of M. de Boisbaudran and his friend for a term of nearly twenty-nine years to be at last suddenly sprung upon the world?

The Periodic Law, it must be remembered, when first announced was not immediately accepted. When Mr. Newlands read his memoir before the Chemical Society (March, 1866), it by no means met with a very enthusiastic reception. One gentleman present even inquired, sarcastically, whether the author "had ever arranged the elements according to the order of their initial letters?" but no one suggested any anticipation.

Then came the announcement by Professors Mendeleeff and L. Meyer of their independent and simultaneous discovery of the same truth. The details were quickly circulated and discussed in the scientific press, and the respective merit of the two savants was for a time a bone of contention. Professor Mendeleeff said (CHEMICAL NEWS, vol. xliii., page 15):—"It is possible that Newlands has, prior to me, enunciated something similar to the Periodic Law, but even this cannot be said of L. Meyer." Yet none of all the authorities who criticised or applauded the new discovery suggests that Newlands, Mendeleeff, and Meyer might all have been anticipated. When M. Lecoq de Boisbaudran made his discovery of gallium he seemed not gratified at the assertion that its existence and its properties had been foreseen in accordance with the Periodic Law. But he made no reference to the "Telluric Screw."

When the successful attempt was made to vindicate the claims of Newlands as the first discoverer, the question was thoroughly re-discussed. But none of the savants who entered into the question ever breathed the name of De Chancourtois. His memoirs were at all times accessible in the *Comptes Rendus*. But no one found in them that meaning which MM. de Boisbaudran and de Lapparent now assert. They certainly contain a proposal to classify the elements with reference to their atomic weights. But we may be permitted to doubt whether they can be fairly considered as the germ of the Periodic Law.

In going over old researches we often find in them matter which we may now regard as a forecast of subsequent discoveries; but there is no sufficient evidence that the author disentangled such matter from accompanying speculations. In the third paragraph from the end of the memoir which we have translated, we find an admission that such has been the case with the writings of M. de Chancourtois. Were his writings placed

textually before us in lieu of the paraphrase of MM. de Boisbaudran and de Lapparent, we should, doubtless, see the reason why they have had no influence on the development of chemical science.

A RECLAMATION OF PRIORITY ON BEHALF OF M. DE CHANCOURTOIS REFERRING TO THE NUMERICAL RELATIONS OF THE ATOMIC WEIGHTS.

By MM. LECOQ DE BOISBAUDRAN and A. DE LAPPARENT

IN 1884 Mr. John Newlands collected under the following title, "On the Discovery of the Law of Periodicity, and on Relations among the Atomic Weights," a number of memoirs which he had previously published in the CHEMICAL NEWS during the years 1864, 1865, and 1866.

The object of the publication was to claim on behalf of Mr. Newlands the priority of the announcement of certain numerical relations which exist among the atomic weights, and which enable us to group the simple bodies in natural families. The author took care to establish that his researches had preceded those of Professor Mendeleeff, and he affirms that he was the first to publish (on July 30th, 1864), a list of all the elements known arranged in the order of their atomic weights.

It is not our intention to contest the merit of the well-known works of Mr. Newlands. Our object is merely to establish that the priority in this matter does not belong to him, as several of the ideas which he believes he was the first to announce in 1864 had been formulated two years previously by a French savant before the Academy of Sciences.

On April 7th, 1862, Béguyer de Chancourtois, at that time Chief Engineer and Assistant Professor of Geology at the School of Mines, presented to the Academy a work entitled: "On a Natural Classification of the Simple or Radicle Bodies entitled 'The Telluric Screw.'" In two subsequent communications (April 21st and May 5th, 1862), the author furnished supplementary details. On October 13th of the same year, he presented to the Academy a lithographic table which summed up all his ideas. Finally, on March 16th, 1863, he concluded with certain general considerations on the numerical character of the simple bodies, as well as on the verifications which spectral analysis might furnish. In this paper is found the very explicit assertion that "the properties of bodies are properties of numbers."

The fundamental idea of the "telluric screw" consists in writing the values of the atomic weights along the generatrix of a vertical cylinder, the circular base of which was divided into 16 equal parts, 16 being the atomic weight of oxygen. If we then trace upon this cylinder a helix with an angle of 45 to its axis, each point of the helix may be considered as the characteristic point of a simple body, the atomic weight of which to the proportional corresponding length of the spiral will be read upon the generatrix which passes by this point.

At each turn the helix returns on one and the same perpendicular at distances from the summit of the cylinder, which are entire multiples of 16, and mark the bodies whose atomic weights conform to this condition. In the same manner the various points of intersection of the helix with any of the 16 principal generatrices, correspond to elements whose atomic weights differ among themselves by 16 or a multiple of 16. Lastly, if after having developed the cylinder upon a plane which transforms the helix into a series of straight parallel segments, we join by a straight line any two points taken upon two segments, after coiling up this right line will produce a secondary helix, and the intersections of this latter with the various turns of the principal helix will mark bodies for which the differences of the atomic weights will be

multiples of a constant quantity. In this manner, the development of the "telluric screw" by simply drawing right lines enables us to show simple numerical relations which it would have been less easy to detect by a mere inspection of the figures.

The relations thus established among the atomic weights correspond for the most part to real analogies in the properties of the corresponding elements. This Chancourtois affirmed in his first memoir, asserting that the "relations of the properties of bodies are manifested by simple relations of position of their characteristic points; and then that each of the helices carried through two characteristic points, and passing by several other points, or merely in their proximity, shows relations of properties of a certain kind, the analogies or the contrasts being manifested by certain numerical orders of succession like the immediate sequence or the alternations at diverse periods.

The "telluric screw" shows at once a classification of the elements according to the order of their atomic weights and the indication of a true periodicity. This is exactly what Mr. Newlands has claimed as especially belonging to him. It is not up to the comparison of atomic periodicity with the musical gamut, of which we cannot deny that it has been, if not proclaimed, at least "interviewed" by Chancourtois. For in his paper of May 5th, 1862, he says expressly: "We cannot refrain from remarking the predominance of the number 7 in the types of the groups occupying the spirals which are most occupied. . . . We arrive easily at the idea of transforming the cylinder upon which the screw is realised into a sonorous tube pierced at the characteristic points." But especially when he published in 1863 a pamphlet containing, along with his memoirs to the Academy some additions which the plan of the *Comptes Rendus* had not allowed him to give in *extenso*. Chancourtois spoke of "direct developments of the system which enable us to perceive at the same time approximations of the series of numerical characteristics to the series of musical sounds, and to that of the bands and rays of the spectrum."

We are far from pretending that the theory of the screw is free from faults, and that the author has not grafted upon his work many considerations which he had better had left in the shade. Several approximations were inaccurate or were strained, and some of them evince a too great part allowed to the imagination. Confiding too much in the virtue of whole numbers (and even of primary numbers), Chancourtois set out with the idea that in the natural series the differences between the atomic weights ought to be constant (an error which, indeed, is also to be met with in the earliest researches of Newlands). If he, indeed, recognised certain gaps in the series of the elements, he endeavoured to fill them up by imagining new varieties of the known simple bodies (which he called *secondary characters*), and which often led him to arrangements little conformable to natural analogies.

Nevertheless, the "telluric screw" was, for its time, an original and even a fruitful conception, for it sufficed to let the author conjecture that the formula of zirconia should probably be written ZrO_2 , that of beryllia BeO , and that of yttria Yt_2O_3 . Further, nothing but the consideration of his helix could have suggested to Chancourtois the slight correction which it was proper to make in the atomic weight of cadmium.

How then does it happen that this publication, inserted in the most widely-circulated scientific journal in the world, the *Comptes Rendus*, has escaped the attention of Mr. Newlands, whose good faith cannot be doubted? It is, we believe, because the text of M. de Chancourtois, somewhat obscure in its conciseness, was not accompanied by any diagram, and that the original memoir circulated by the author had not a sufficiently wide distribution. We have therefore thought proper to join to this memoir (arranging it for simplicity in two parallel

columns which should be joined end to end), a reduction of that part of the graphic table which extends from hydrogen to tellurium. The secondary helix has been traced which passes by sulphur, iron, selenium, tellurium, and which, if produced, would extend to gold.—*Comptes Rendus*, vol. cxlii, p. 77.

A NATIONAL CHEMICAL SOCIETY IN AMERICA.

THE second general meeting of the American Chemical Society was held in the University of Pennsylvania, at Philadelphia, December 30th and 31st, 1890. Professor GEORGE F. BARKER, M.D., President. The attendance was large, the arrangements for both business and for entertainment were excellent, and many valuable papers were read which will be published in the *Journal*.

Under the auspices of the American Chemical Society a conference of chemists, representing seven different bodies, assembled to consider the formation of a National Organisation of American Chemists. The societies or bodies represented by delegates were the following:—(1) Chemical Section of the American Association for the Advancement of Science. (2) American Chemical Society. (3) Chemical Section of the Franklin Institute, Philadelphia. (4) Chemical Section of the Brooklyn Institute. (5) Association of Official Agricultural Chemists. (6) Chemical Society of Washington, D.C. (7) Manufacturing Chemists' Association of the United States. The newly-formed Chemical Society of Cincinnati was not represented.

Professor Albert B. Prescott, of Ann Arbor, Michigan, President-Elect of the American Association for the Advancement of Science, was called to the chair, and Dr. H. Carrington Bolton, of New York, was appointed Secretary.

After a prolonged and interesting discussion the following resolutions were adopted.

Resolution 1.—It is desirable that an American Association of Chemists be formed to embrace all existing American Chemical organisations.

Resolution 2.—Resolved, That this conference recommend to all existing American Chemical organisations that they call a meeting of their bodies to be held in Washington, D.C., in connection with the meeting of the American Association for the Advancement of Science for 1891, and that each of these organisations be requested to appoint a committee, or to continue their present committee for the further discussion of the subject submitted to the conference now in session.

Resolution 3.—Resolved, That this general conference committee, composed of the present sub-committees, or such others as may be appointed by the several organisations, be called together at as early a time as practicable before the joint meeting recommended in Resolution 2.

Resolution 4.—Resolved, That meanwhile, each sub-committee through its chairman, by correspondence or otherwise, shall formulate such modifications of the Constitution of the American Chemical Society as it shall deem necessary to adapt it to the requirements of the Association proposed.

Resolution 5.—Resolved, That the chairmen of these sub-committees shall then, so far as possible, harmonise the views embodied in these reports of their several organisations, and shall have printed, for presentation at the joint meeting, a report, or minority and majority reports, on a constitution for the proposed Association of American Chemists.

The secretary of the conference was desired to communicate the above resolutions to Scientific Journals with a view to obtain a wide publication of the same.—Adjourned to meet at the call of the chairman.—H. CARRINGTON BOLTON, *Secretary of the Conference*,

ELECTRICITY
IN TRANSITU:
FROM PLENUM TO VACUUM.*

By WILLIAM CROOKES, F.R.S.,
President of the Institution of Electrical Engineers.

Introduction.

WHILST steadily bearing in mind that I have the honour to address a Society, not only of physicists, but of Electrical Engineers, I shall not, I hope, be out of order in venturing to call your attention to a purely abstract phase of Electrical Science. Numberless instances show that pure research is the abundant source from which spring endless streams of practical applications. We all know how speculative inquiry into the influence of electricity on the nervous system of animals led to knowledge of current electricity, and ultimately to the priceless possession of the telegraph and the telephone. The abstract study of certain microscopic forms of parasitic vegetable life has enabled us to give to fermented solutions of sugar the exact flavour and aroma of the most highly prized wines, and probably, ere long, will put us in a position to increase at will the fertility of the soil. In a different direction the same class of abstract researches applied to medical science has brought us within measurable distance of the final conquest over a large class of diseases hitherto incurable; and without egotism I may, perhaps, be allowed to say that my own researches into high vacua to some extent have contributed to the present degree of perfection of the incandescence lamp. Surely, therefore, whilst eagerly reaping and storing the harvest of practical benefits, we must not neglect to scatter more seed for future results, perchance not less wonderful and valuable.

In another respect I deviate to some extent from the course taken by many of my predecessors. I am about to treat electricity, not so much as an end in itself, but rather as a tool, by whose judicious use we may gain some addition to our scanty knowledge of the atoms and molecules of matter and of the forms of energy which by their mutual reactions constitute the universe as it is manifest to our five senses.

I will endeavour to explain what I mean by characterising electricity as a tool. When working as a chemist in the laboratory, I find the induction spark often of great service in discriminating one element from another, also in indicating the presence of hitherto unknown elements in other bodies in quantity far too minute to be recognisable by any other means. In this way, chemists have discovered thallium, gallium, germanium, and numerous other elements. On the other hand, when examining electrical reactions in high vacua, various rare chemical elements become in turn tests for recognising the intensity and character of electric energy. Electricity, positive and negative, effect respectively different movements and luminosities. Hence the behaviour of the substances upon which electricity acts may indicate with which of these two kinds we have to deal. In other physical researches both electricity and chemistry come into play simply as means of exploration.

In submitting to you certain researches in which electricity is used as a tool, or as a means of bringing within scope of our senses phenomena that otherwise would be unrevealed, I must for a moment recal to your minds the now generally accepted theory of the constitution of matter.

Kinetic Theory of Gases.

Matter, at its ultimate degree of extension, is conjectured to be not continuous, but granular. Maxwell illustrates this view as follows:—To a railway contractor driving a tunnel through a gravel-hill the gravel may be viewed as a continuous substance. To a worm wriggling through gravel, it makes all the difference whether the

creature pushes against a piece of gravel or directs its course between the interstices. To the worm, therefore, gravel seems by no means homogeneous and continuous.

With speculations as to the constitution of liquid and solid matter I need not trouble you, but will proceed at once to the third or gaseous state of matter.

The kinetic theory of gases teaches that the constituent molecules dart in every possible direction with great but continually varying velocities, coming almost ceaselessly in mutual collision with each other. The distance each molecule traverses without hitting another molecule is known as its *free path*; the average distance traversed without collision by the whole number of molecules of a gas at any given pressure and temperature is called the *mean free path*. The molecules exert pressure in all directions, and are only restrained by gravitation from dissipating themselves into space. In ordinary gases, the length of the mean free path of the molecules is exceedingly small compared with the dimensions of the vessel, and the properties we then observe are such as constitute the ordinary gaseous state of matter, which depend upon constant collisions. But if we greatly reduce the number of molecules in a given extent of space the free path of the molecules under electric impulse is so long that the number of their mutual collisions in any given time in comparison with the number of times they fail to collide may be disregarded. Hence, the average molecule can carry out its own motions without interference. When the mean free path becomes comparable to the dimensions of the containing vessel, the attributes which constitute gaseity shrink to a minimum, the matter attains the ultra-gaseous or "radiant" state, and we arrive at a condition where molecular motions under electrical impulse can easily be studied.

The mean free path of the molecules of a gas increases so rapidly with progressive exhaustion, that whilst that of the molecules of air at the ordinary pressure is only 1-10,000th of a millimetre, at an exhaustion of a hundred-millionth of an atmosphere—a point (which, with present appliances, is easy to attain) corresponding to the rarefaction of the air 90 miles above the earth's surface—the mean free path will be about 30 feet; whilst at 200 miles above the earth it will be 10,000,000 miles, and millions of miles out in the depth of space it will become practically infinite. I could go on speculating in spite of Aristotle, who said:—"Beyond the universe there are neither space, nor vacuum, nor time."

In discussing the motions of molecules we have to distinguish the *free path* from the *mean free path*. Nothing is yet known of the *absolute* length of the free path nor of the *absolute* velocity of a molecule. For anything we can prove to the contrary, these values may vary almost from zero to infinity. We can deal only with the *mean free path* and the *mean velocity*.

The Vacuum Pump.

As most of the experiments I put before you to-night are connected with high vacua, it is not out of place to refer to the pump by means of which these tubes are exhausted. Much has been said lately in recommendation of the Geissler pump and its many improvements, but I am still strongly in favour of the Sprengel, as with it I have obtained greater exhaustion than with any other. I should like to point out that the action does not stop when we cease to see air specks passing down the tubes but continues long after this point has been passed. Neither is the non-conducting vacuum, so easily obtained by the Sprengel pump, due in any way to the presence of mercury vapour, since non-conduction can be obtained just as rapidly when special precautions have been taken to keep mercury vapour out of the tubes.

One of the great advantages of the Sprengel pump over all others lies in the fact that its internal capacity need not exceed a few cubic centimetres, and there is, therefore much less wall surface for gases to condense upon. I have brought the very latest modification of this form

* Inaugural Address delivered January 15th, 1892.

of pump here to-night, and you will have an opportunity of seeing it in action and of measuring with the McLeod gauge the rarefaction it produces.*

* My measurements of high vacua have all been taken with the beautiful little gauge devised by Professor McLeod. Unmerited discredit has recently been cast on this gauge, the principal fault alleged being its inability to distinguish between the tension of the permanent gas and that of the mercury vapour present. Now it is evident that, under ordinary circumstances, the tension of mercury vapour may be disregarded, as it will be the same on both sides of the gauge; and it will be only in cases where no mercury is present on one side of the gauge that a slight error is introduced. It is, however, very difficult to devise and successfully experiment with apparatus in which a trace of mercury vapour shall not enter, and it is not

The Passage of Electricity Through Rarefied Gas.

The various phenomena presented when an induction spark is made to pass through a gas at different degrees of exhaustion point to a modified condition of the matter at the highest exhaustions. Here are three exactly similar bulbs, the electrodes being aluminium balls, and the internal pressures being respectively 75 m.m., 2 m.m., and 0.1 m.m. If I pass the induction current in succession through the bulbs, you will perceive in each case a very different luminous phenomena. Here is a slightly exhausted tube (Fig. 1), like the first in the series just exhibited (75 m.m.), the induction spark passes from one

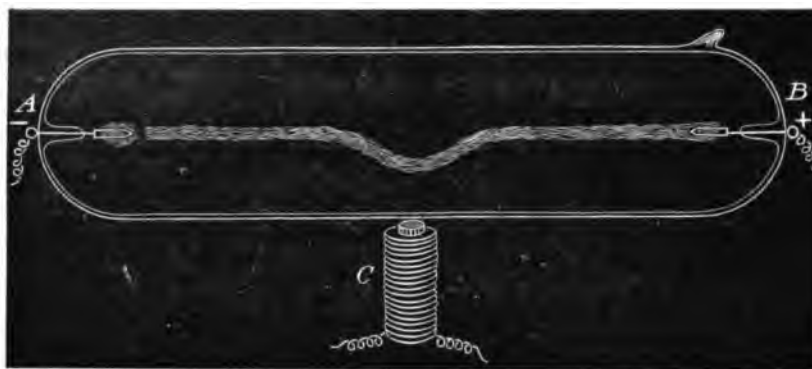


FIG. 1.—P. = 75 m.m.

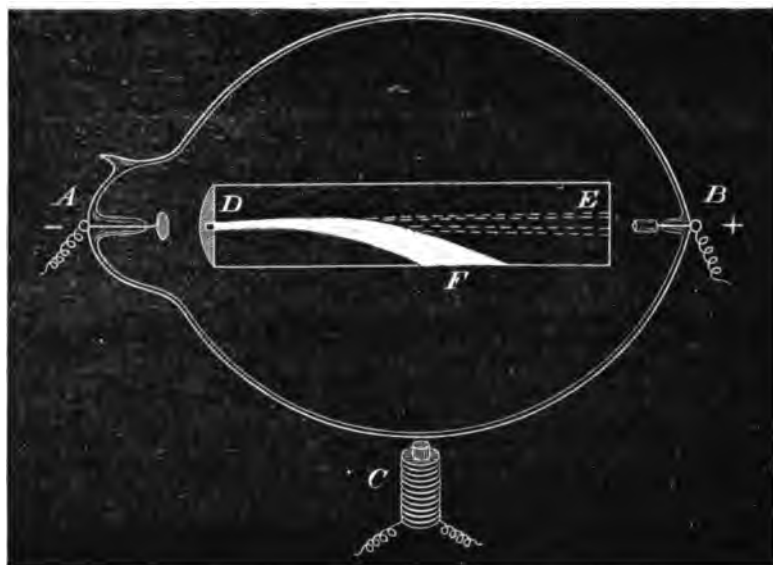


FIG. 2.—P. = 0.1 m.m.

likely that an experimentalist who would be working with such mercury-free apparatus would attempt to use the gauge without remembering that in this special case the indications would be incorrect. To use the McLeod gauge requires much patience and some amount of experience, but I have always found it trustworthy to register exhaustions far beyond the millionth of an atmosphere. I can adduce circumstantial evidence of the accuracy of its readings at these high vacua. In the year 1881 I read a paper before the Royal Society on "The Viscosity of Gases at High Exhaustions" (*Phil. Trans.*, 1881, p. 387), and illustrated my results in three large diagrams, on which I plotted the experimental results obtained at rarefactions up to 0.02 millionth of an atmosphere, giving curves comparing the decrease in viscosity with that of the repulsion resulting from radiation, at the different pressures. Now these curves, in the case of air for instance, are perfectly regular and uniform in their falling off, and it is evident that this could not have been the case unless the ordinates

end to the other, A, B, and the luminous discharge is seen as a line of light, acting as a flexible conductor. Under the tube I have an electro-magnet, C, and on making con-

representing viscosity and the abscissæ representing pressure were equally accurate. I am satisfied that, within narrow limits, the ordinates of viscosity are correct to the highest point, and the conformity of experiment to theory in the shape of these curves is a conclusive proof that, at as high an exhaustion as 0.02 M., the McLeod gauge is to be trusted to give accurate results within 2 per cent of the truth. To give some idea what these high exhaustions mean I may mention that the highest measured exhaustion—0.02 M.—bears the same proportion to the ordinary pressure of the atmosphere that a millimetre does to 30 miles, or in point of time, that one second bears to 20 months.

that the line of light dips in the centre down to the poles of the magnet, and then rising again proceeds in a straight line. On reversing the current the line of light curves upwards. Notice that the action of the magnet in this case is only local.

In a highly exhausted tube the action is quite otherwise. Such a tube is before you (Fig. 2), and in it I have carried the exhaustion to a high point (0.1). I pass the induction current and you perceive the electrified molecules, like the line of light in the first tube, also move in straight lines, and make their path apparent by impinging on a phosphorescent screen, &c. If, however, I submit them to the action of a magnet, &c., their behaviour is different. The line dips down to $\mathbf{F}$, but does not recover itself. It seems that in the tube first shown we have to do with the average behaviour of the molecules of gas in its totality. In the second case, where the gas has been greatly attenuated, we are merely concerned with the be-

haviour of the individual molecules of which it was originally composed.

Hence mere differences in speed suffice to resolve a multitude of passengers into alternating gaps and knots.

Instead of observing moving men and women, suppose we experiment on little particles of some substance, such as sand, approximately equal in size. If we mix the particles with water in a horizontal tube and set them in rhythmic agitation, we shall see very similar results, the powder sorting itself with regularity into alternate heaps and blank spaces.

If we pass to yet more minute substances we observe the behaviour of the molecules of a rarefied gas, when

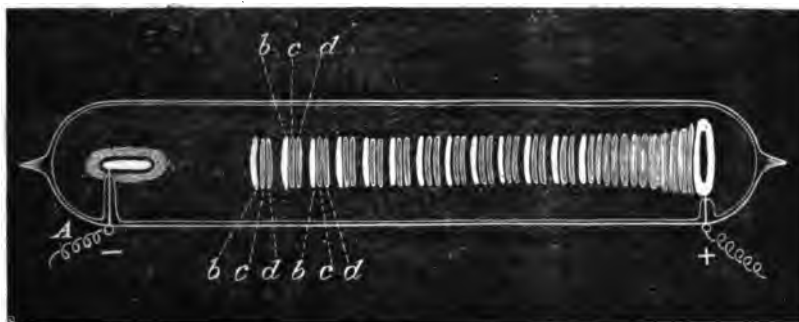


FIG. 3.— $P = 2$ m.m.

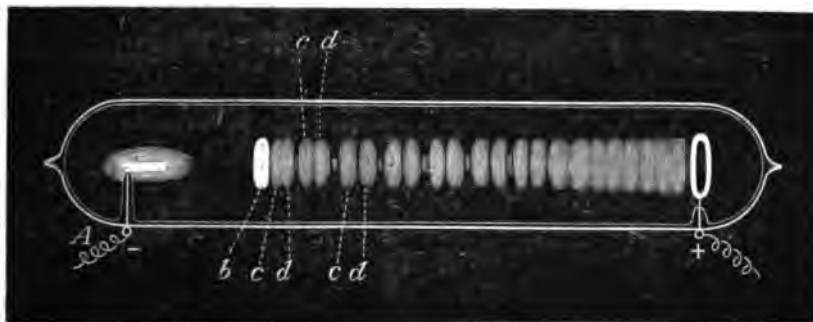


FIG. 4.— $P = 2$ m.m.

haviour of the individual molecules of which it was originally composed.

The Stratified Discharge.

When the gas is rarer than is necessary to give the flexible line of light, as shown in the first experiment, the luminosity is plainly discontinuous, or, as it is termed, stratified.

A very good illustration of this fact may be taken from the moving crowd in any much frequented street—say Fleet Street. If at some time when the stream of traffic runs almost equally in both directions, we take our stand at a window from which we can overlook the passing crowd, we shall notice that the throng on the foot-way is not uniformly distributed, but is made up of knots—we might almost say blocks—interrupted by spaces which are comparatively open. We may easily conceive in what manner these knots and groups are formed. Some few persons walking rather more slowly than the average rate slightly retard the movements of others whether travelling in the same or in an opposite direction. Thus a temporary ob-

struction is created. The passengers behind catch up to the block and increase it; and those in front, passing on unchecked at their former rate, leave a comparatively vacant space. If a crowd is moving all in the same direction the formation of these groups becomes more distinct. With vehicles in crowded streets, the result, as everyone may have remarked, will be the same.

Party-coloured Stratifications.

As another illustration of stratifications in a moderately exhausted tube ($P = 2$ m.m.), I will take the case of hydrogen prepared from zinc and sulphuric acid after being passed through various purifying agents, dried in the usual manner, and exhausted with a mercury pump (Fig. 3). I pass the induction current, and we see that the stratifications are tri-coloured, blue, pink, and grey. Next the negative pole $\mathbf{A}$ is a luminous layer, then comes a dark interval or Faraday's dark space (see below), and after this are the stratifications, the front component ($\mathbf{b}$) of each

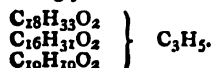
group blue, the next (c) pink, and the third (d) grey. The blue disks are somewhat erratic. At a certain stage of exhaustion all the blue components of the stratifications suddenly migrate to the front, forming one bright blue disk, and leaving the pink and grey components by themselves. The tube before you (Fig. 4) is at this particular stage of exhaustion, and on passing the current you observe the blue disk only (b) is in front. When the tube contains a compound gaseous residue of this kind, the form of stratifications can be very considerably altered by varying the potential of the discharge. This alteration in the forms of stratification was first pointed out by Cassiot (1865, "B.A. Abstracts," p. 15), who gave very full descriptions and drawings of the alterations produced by putting in resistances of various lengths of distilled water. That the alteration depends simply upon the difference of potential the following experiment pretty clearly shows:—Here is a tube giving on my coil the coloured stratification usually attributed to the presence of residual hydrogen, but which I find is due to a mixture of hydrogen, mercury, and hydrocarbon vapours. Now by altering the brake so as to produce frequent discharges of lower potential, you see the stratifications gradually change in shape and become all pink; again altering the brake so as to send less rapid discharges at a much higher potential, once more we get the coloured stratifications. When in this state, if we introduce a water resistance into the circuit so as to damp down the potential, exactly the same thing happens. The blue disk is caused by mercury; its spectrum is that of mercury only, without even a trace of the bright red line of hydrogen. Experiments not yet finished make it very probable that the pink disks are due to hydrogen, and that the grey disks indicate carbon. The tube you have just seen contains nothing but hydrogen, mercury, and a minute trace of carbon; but with all the resources at my command I have not been able to get hydrogen quite free from impurity. Indeed I do not think absolutely pure hydrogen has ever yet been obtained in a vacuum tube. I have so far succeeded as to completely eliminate the mercury, and almost completely to remove the trace of carbon. On the table is such a tube giving uniformly pink stratifications and showing no blue or grey disks with any potential of current.

(To be continued).

COMPOSITION OF BUTTER FAT.

By WILLIAM JOHNSTONE, Ph.D., D.Sc., F.I.C., F.C.S.

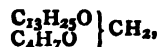
FOR some considerable time now the insoluble fatty acids of butter fat have been taken as varying from 87.5 to 89.5 per cent, and in some extreme cases even to 90 per cent. In the month of June, 1890, two samples of butter came into my hands, and in course of analysis, my attention was particularly directed to them on account of the low results obtained for insoluble fatty acids with corresponding highness in the soluble fatty acids, so I was induced to further examine them in the hope that I should be able to account for the apparent abnormal figures I had obtained, namely, 85.68 and 86.25 per cent, as they were undoubtedly genuine, the addition of cocoa-nut oil being out of the question. That investigation has resulted in establishing the fact that a butter fat yielding 85.81 per cent of insoluble fatty acids is a definite chemical compound, a compound tri-glycerin of the following formula:—



the iso-oleo-palmito capriate of glycerin.

Up to the present time it was by no means certain that butter fat did really contain normal oleic acid or stearine, and my results now confirm the accuracy of that suspicion. A butter fat, therefore, yielding 85.81 per cent of insoluble fatty acids is entirely devoid of stearine, and what was

previously considered to be oleic acid now proves to be iso-oleic acid—



or butro-methene, tridacotic acid.

Furthermore, genuine butter fats yielding insoluble fatty acids above 85.81 per cent do not contain stearic acid (?) as is generally supposed, but nondecatoic acid, the next higher acid of the series, as a glyceride. Butter fat then becomes a mixture of iso-oleo-palmito capriate of glycerin and tri-nondecatoic of glycerin in varying proportions, a compound complicated tri-glyceride.

The following represent a butter fat of that description:—

Fatty acids.				
$\left. \begin{array}{l} \text{C}_{18}\text{H}_{33}\text{O}_2 \\ \text{C}_{16}\text{H}_{31}\text{O}_2 \\ \text{C}_{10}\text{H}_{19}\text{O}_2 \end{array} \right\}$	C_3H_5	62.47	=	53.61
$\left. \begin{array}{l} \text{C}_{19}\text{H}_{37}\text{O}_2 \\ \text{C}_{19}\text{H}_{37}\text{O}_2 \\ \text{C}_{19}\text{H}_{37}\text{O}_2 \end{array} \right\}$	C_3H_5	$\frac{37.53}{100.00}$	=	$\frac{36.00}{89.61}$

Fatty acids actually found .. 89.95

From the above, it becomes evident that another acid radicle might replace one of nondecatoic acid, and that occurs in the following butter:—

Fatty acids.				
$\left. \begin{array}{l} \text{C}_{18}\text{H}_{33}\text{O}_2 \\ \text{C}_{16}\text{H}_{31}\text{O}_2 \\ \text{C}_{10}\text{H}_{19}\text{O}_2 \end{array} \right\}$	C_3H_5	53.21	=	45.66
$\left. \begin{array}{l} \text{C}_{19}\text{H}_{37}\text{O}_2 \\ \text{C}_{19}\text{H}_{37}\text{O}_2 \\ \text{C}_7\text{H}_{14}\text{O}_2 \end{array} \right\}$	C_3H_5	$\frac{46.79}{100.00}$	=	$\frac{44.50}{90.16}$

Fatty acids actually found .. 90.00

The radicle of oenanthylic acid replacing one of the nondecatoic acids in the tri-glyceride, and forming the dinondecatoic-oenanthylic of glycerin.

I append the following formula in support of my theory. Thus:—

	Theory.		Theory.	Found.
$\text{C}_{13}\text{H}_{25}\text{O}$	.. 26.34	$\left. \begin{array}{l} \text{C}_{13}\text{H}_{25}\text{O} \\ \text{CH}_2 \\ \text{C}_4\text{H}_7\text{O} \\ \text{C}_{13}\text{H}_{25}\text{O}_2 \\ \text{C}_{10}\text{H}_{19}\text{O}_2 \\ \text{C}_3\text{H}_5 \end{array} \right\}$	$\text{C}_{13}\text{H}_{25}\text{O}$	28.60
CH_2	.. 1.7		CH_2	2.13
$\text{C}_4\text{H}_7\text{O}$	.. 9.45		$\text{C}_4\text{H}_7\text{O}_2$	11.76
$\text{C}_{13}\text{H}_{25}\text{O}_2$	.. 34.09		$\text{C}_{16}\text{H}_{33}\text{O}_2$	34.22
$\text{C}_{10}\text{H}_{19}\text{O}_2$	.. 22.86		$\text{C}_{10}\text{H}_{20}\text{O}_2$	22.99
C_3H_5	.. 5.47		$\text{C}_3\text{H}_5\text{O}_3$	12.30
	99.98	Upon saponification yield		112.00

The ultimate separation of the fatty acids is still in hand, and I refrain from giving results until I am able to give a correct process for the separation of the same; but results have been obtained near enough to prove the correctness of the theory. Butter analysis is, therefore, now placed on a satisfactory basis, and if the analyst be fortunate enough to detect stearic acid in a sample of butter, he need have no hesitation in certifying the addition of animal fat other than butter, or at least to a fat containing stearic acid.

THE FILTRATION OF NATURAL WATERS.*

By THOMAS M. DROWN,
Member Boston Society Civil Engineers.

(Concluded from p. 48).

THE surface waters used to supply London from the Thames or the Lea are filtered by the method of continuous filtration, a surface of one hundred acres being required for the purpose. The thickness of sand differs

* From a Paper read January 15, 1890. Reprinted in part from the *Journal of the Association of Engineering Societies*.

with the different companies supplying the city with water, from two feet at the East London and Grand Junction Companies to four and a half feet at the Chelsea Company, and the rate of filtration per hour in imperial gallons per square foot of filtering surface is two and one-sixth with the Lambeth Company, to one and a half gallons with the Southwark and Vauxhall Company. Two and a half gallons, or five vertical inches an hour (which is seldom attained), is considered the maximum consistent with good clarification. Complete analyses are made of the water supplied to the metropolis by the different companies. Some of the determinations, as for instance colour, and the amount of permanganate to oxidise the organic matter are made daily; other chemical determinations are made weekly. The monthly determinations made by Dr. Percy F. Frankland, of the bacteria in the waters of the different companies have been suspended since December, 1888. The average reduction of the number of micro-organisms present in the waters of the Thames and Lea, was in 1887 97.6 per cent in the case of the Thames, and 93.9 in the case of the Lea. "If," says the report on the metropolitan supply for December, 1888, "these figures could be accepted as at all representing the degree of security given to consumers of the waters of those rivers by preliminary filtration, it is evident that the views on this subject acquired by a consideration merely of the results of comparative chemical analysis of filtered and unfiltered waters would have to be considerably modified, and the character of the water supply would be correspondingly raised in the public estimation. Further, if the results obtained from month to month could be relied on as an index to the effect of filtration in eliminating objectionable matters from the water, the bacteriological method would seem to afford a delicate and easily applied test of the working efficiency of the filter."

The average numbers of bacteria in the water of the Thames is generally less than in the Spree at Berlin; thus during the year ending December, 1887, the highest number in November was 81,000, and the lowest in June was 2200, the average for the year being 21,492.

The only filtering plant in this country that I know of which at all compares with the plants in Europe, is that at Poughkeepsie, where the Hudson River water is converted into good clear water, though not absolutely free from colour. Mr. Fowler, the superintendent of the works, writes me with regard to the details of the filtration:—"Our usual rate of filtration is about six inches per hour, vertically, and this we regard as the maximum of efficiency, although we can sometimes do good work, so far as clarifying is concerned, at double that rate, and at other times are unable to do good work at one half that rate, although the latter condition is exceptional. Very much depends upon the condition of the water in the river. The depth of water on the sand varies from one to three or four feet, and the difference of level between the surface of the water on the beds and that in the intermediate basins is usually two to four or five feet."

The rapid filtration of water through coarse gravel is not unfrequently carried out at water works to remove the larger particles floating in the water. When a filter of this kind is cleaned, it is surprising to see the amount of fine dirt of all kinds that has been intercepted by the coarse material. Filters of this character do not pretend to purify the water in the sense of removing bacteria or in oxidising the organic matter, but they are useful just to the extent to which they clarify the water and thereby improve its appearance.

The American system of filtering large quantities of water may be said to be the mechanical filters working under pressure. These filters are composed of four or five feet of moderately fine sand (some have also a mixture of coke), enclosed generally in boiler-iron cases. They work with tremendous rapidity, sometimes over a hundred vertical feet an hour, but forty feet is said by

some to be the highest rate consistent with good filtration. In this system alum is generally added to the water as a coagulant. Its effect in very small amount is quite remarkable—say a grain to a gallon, or even less—in retaining the solid matters of the water in the sand of the filter. The alum is decomposed by the carbonates in the water, and hydrate of alumina is precipitated. This is a gelatinous and slimy substance, and immediately surrounds the algæ, clay, and anything else that may be suspended in the water, and the sand retains this coagulated mass. Alumina has also the effect of taking the colour out of water, so that clear, colourless water may be obtained by this process from swampy waters full of growing algæ with almost incredible rapidity.

These filters are in very general use in paper mills and other industrial works where a clear, colourless water is needed, and where a coloured turbid river water is the only natural supply available. They have also been introduced into some cities of considerable size, as, for instance, Long Branch, Chattanooga, and Atlanta, and they are said to give water that is satisfactory to those who use it. The objection to the system is the use of alum. If all the alum used were decomposed in the few seconds that it takes the water to pass through the filter, so that no undecomposed alum passed into the filtered water, there might be no objection to its use, but this is not always the case. The amount of alum used is ordinarily small, and it is claimed that if it even all went into the filtered water it would not injure it for drinking. This may be so, but the prejudice that exists against drinking water which has been treated with "chemicals" is so strong that it is not likely that any system using a coagulant in a soluble form will find general acceptance. Under some conditions, when the water has high colour with much suspended matter, the alum has to be increased largely to give good results. I have known as high as seventeen grains to the gallon to be used with a very bad swampy water.

In this connection should be mentioned the spongy iron filter of Bischof, which gives most excellent results both in taking out suspended matters from the water, including the bacteria, and also decreases the hardness of the water. This filter has been used on the small scale in houses, and also on the large scale in Antwerp, to decolourise and otherwise purify the water of that city. The filter is composed of finely-divided metallic iron made by reducing iron ore by means of carbon at a temperature below fusion. Its action was not understood for a long time, and the mystery that surrounded it was an additional recommendation for it. The rationale of its working seems to be this, namely, that the iron being in a very finely-divided state is dissolved to a slight extent by the combined action of the oxygen and carbonic acid in the water, and the ferrous carbonate thus produced is further oxidised, forming hydrate of iron, and then this acts as a coagulant just as the alumina hydrate does. The system was said to be too expensive on a large scale, and it has now been replaced at Antwerp by the Anderson process, in which the dark water is made to pass through a long revolving iron cylinder in which there is a large quantity of fragments of cast iron. These fragments of iron in their friction one on the other are abraded, minute particles are broken off which are dissolved in the way above described. The water coming from the revolving cylinder is exposed to the air, the iron oxidises and precipitates, combines with the colouring matter in the water, encloses the solid particles, and is then filtered out through sand. The process is said to work satisfactorily and give clear, colourless water. There is no objection to this use of iron as a coagulant, provided that it is all oxidised and precipitated, and none is carried in solution into the filtered water; but this takes time.

Both alum and iron salts have a tendency to sterilise water. Their action may be both direct by killing the bacteria, and indirect by removing them with the precipitated alumina or iron hydrate. If a drop of a solution of

alum or of iron chloride be added to a gallon of turbid water, it will become perfectly clear in the course of a few hours, the alumina or iron hydrate, which is formed in the water, settling to the bottom and carrying all the suspended matters with them. It has been proposed to clarify Mississippi water by adding a very small quantity of an iron solution to the water in the settling basins.

I have laid some weight on the desirability of following nature's processes in the purification of impure waters. Neither the American system, with its mighty rush of waters, or the European system, with its calm, steady, and deliberate flow, finds any analogy in nature. In the rapid-working mechanical filters a coagulant is used to grasp and hold the suspended matter; in the continuously working filter beds the bacteria are put to a novel use in retaining the solid matter on the sticky surface of the sand.

Nature uses these methods also; she removes colour by means of clay in the soil and intercepts mechanically in the bacteria-laden soil all the solid matter in the water, but she goes further than this, and, giving the bacteria full play, breaks up the organic compounds and leaves no trace of their existence behind. To do this, time is needed. "The bacteria of nitrification," as Dr. Smart has well said, in referring to the systems of rapid filtration, "cannot be harnessed to the work of artificial filtration."

The rate at which nature works may be expressed in the amount of rainfall. If we take the rainfall at fifty inches, and assume that even half of this sinks into the ground (a very high estimate), we have twenty-five inches yearly on a square foot of surface. The amount of water which goes through the Berlin filters, at a rate of four inches an hour, is more than 1250 times this amount. If we wish to imitate the process by which nature makes its springs, we must pour the water from river or lake which we wish to filter intermittently on the surface of ground which is favourable for this purpose. The favourable conditions are these:—The ground must be sufficiently porous to allow the ready flow of water through it, and it must have such relations to the strata below as will enable us to collect the water at some lower level. It would not profit us much to pour the water on to a gravel bed if we could not find it again after it had been filtered. If the natural conditions for this purpose are not favourable, drains would have to be put in at suitable depths to collect the filtered water. Water purified in this way would in no wise differ from natural spring water, provided that the amount of water applied did not exceed the capacity of the filtering area.

The question of the maintenance of the purity of the water supplies of large cities, which are dependent upon surface waters, is daily becoming more urgent in this country as the population becomes more dense on the collecting areas, and the protection of streams against pollution becomes more and more difficult. The radical remedy in such cases is to take water from another and, usually, more distant region, which, it is probable, will never become thickly settled. But in filtration, both intermittent and continuous, when intelligently conducted, we have a substitute which can give as clear, colourless, and, we have good reason also to suppose, safe drinking water.

The Production of Higher Alcohols During the Alcoholic Fermentation.—L. Lendet. — In view of the author's results, it is impossible to admit that the higher alcohols are exclusively produced by the normal fermentation of sugar, and their formation must be chiefly sought for elsewhere. Their origin may be traced to the development of a micro-organism, the action of which at the outset of fermentation is smothered by the action of the yeast, but which resumes its activity when the yeast has completed its task.—*Comptes Rendus*, vol. cxii., No. 2.

THE SPECIFIC GRAVITY OF A LIQUID, A FUNCTION OF ITS BOILING-POINT AND MOLECULAR WEIGHT.

By A. E. RICHARDSON, Assoc. Inst. Elec. Eng.

THE boiling-point of a liquid is to some extent dependent upon the molecular weight of that liquid. This fact is best observed in the case of the homologous series in organic chemistry, in which a fairly constant rise in the boiling-point occurs for a constant increase of molecular weight. Nevertheless, between *specific gravity* and the temperature of ebullition, no definite relations seem to have been observed.

If, by a new mode of procedure, some connection were found to exist between these two quantities—boiling-point and specific gravity—there is no reason to doubt that a material aid would be rendered to the solution of the more important problem, namely, the dependence of specific gravity upon molecular weight. In this paper, only those liquids which possess a specific gravity greater than unity have been examined.

Under what conditions must a liquid be placed that its specific gravity may appear as a function of its boiling-point? The boiling-points, pure and simple, apparently have no connection whatever with the specific gravities, and thus some other temperature must be considered. Imagine the case of a liquid heated to temperatures far above its boiling-point. Also conceive that ebullition has by some means been prevented. Under such circumstances it is palpable that the specific gravity of the liquid will have much decreased, taking it for granted that the liquid would continue expanding. At some temperature, constant for each liquid, the specific gravity would at last assume unit value. Here then is a new condition of liquid matter, namely, the temperature at which each given liquid attains unit specific gravity.

To arrive at these temperatures two measurements are required for every liquid. We must know (1) the specific gravity at some given temperature, and (2) the rate of expansion between 0° and the boiling-point.

In the following tables these temperatures have been calculated for a few liquids. The specific gravities and rates of expansion were taken from Professor Thorpe's paper on specific volume (*Trans. Chem. Soc.*, 1880).

In this table m = molecular weight, T = unit specific gravity temperature (Centigrade), T_a = absolute temperature of unit specific gravity, t = boiling-point (Centigrade), and t_a = absolute temperature of boiling.

With inorganic compounds we have the following results. (See Table, p. 60).

The values of T were calculated from the equation for liquid expansion, $V = 1 + at + bt^2 + ct^3$. The values of a , b , and c are given in the paper above mentioned, for all temperatures between 0° and the boiling-point for each liquid. The equations are here assumed to hold true for temperatures above the boiling-points. Curves I. and II. are obtained by plotting the values of specific gravity as abscissæ, and temperatures of unit specific gravity as ordinates, from Tables I. and II. respectively. The curves show that specific gravity is a function of the temperature of unit specific gravity. Since the rates of expansion of the various liquids are so extremely variable, no such relation could have been predicted.

The values of $\frac{T}{m}$ are very uniform, and many of them closely approximate to the number 2. It seems extremely probable that if a large number of liquids were examined, they might admit of division into groups, such that for each group a constant value of $\frac{T}{m}$ would be obtained. Such a division would at first be purely empirical. The reason of such a grouping would possibly appear when a

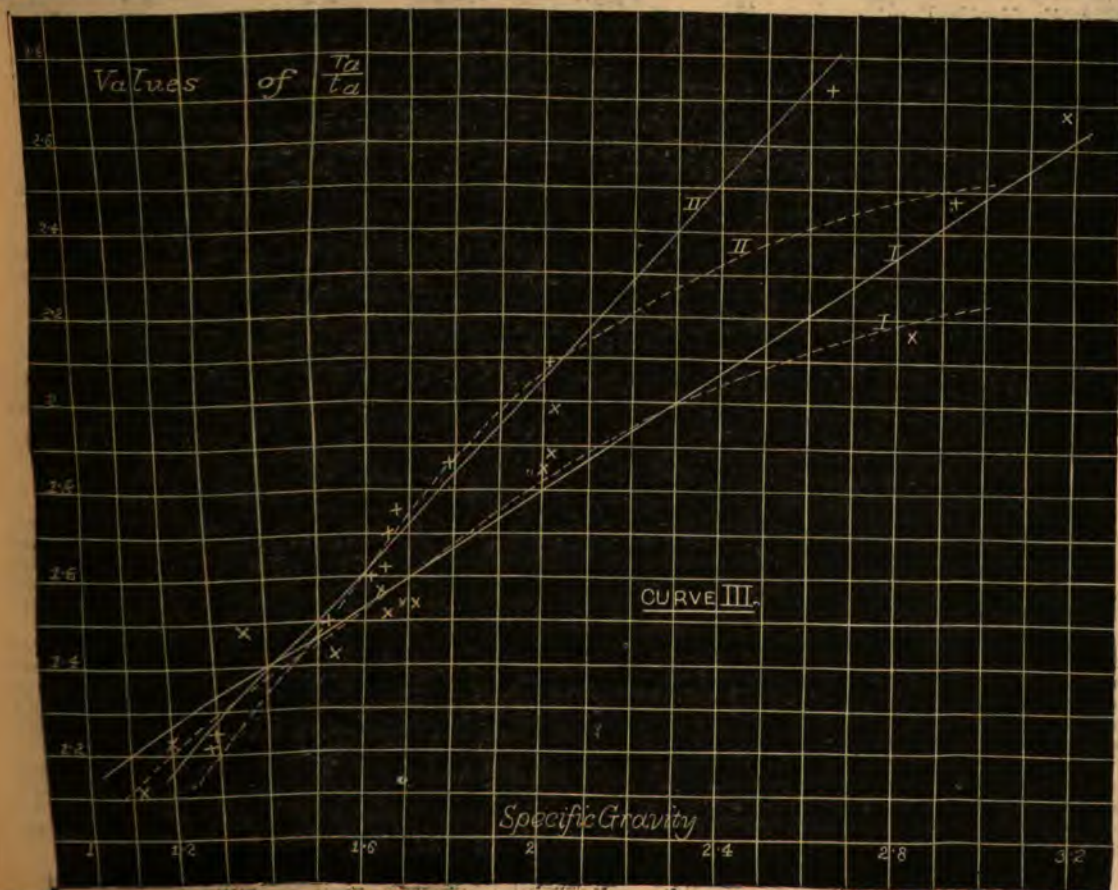
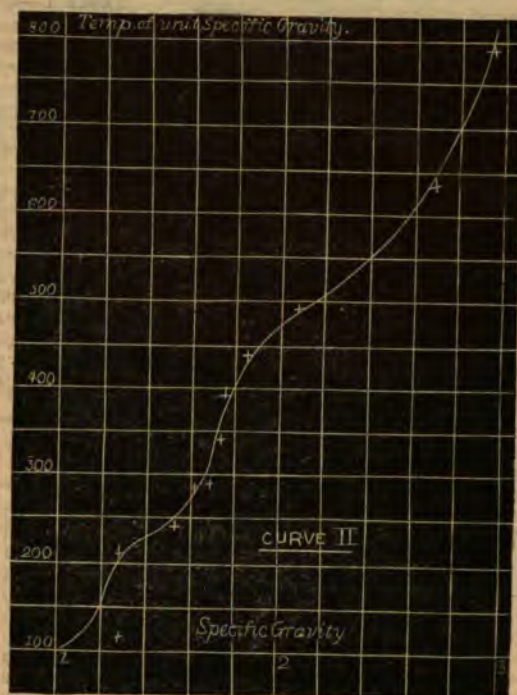
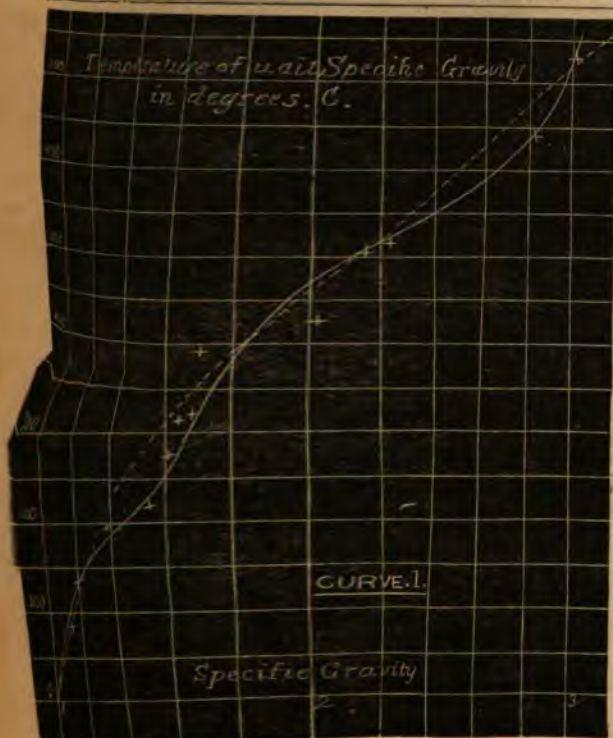


TABLE I.—Organic Compounds.

Formula.	Molecular weight.	Unit specific gravity temp.	Specific gravity.	Boiling point.	$\frac{T}{m}$	$\frac{T}{f}$	$\frac{T_a}{f_a}$
C_2H_5OCl	78.5	84°	1.13773	50.7°	1.07	1.65	1.13
CH_3CHCl_2	98.7	136	1.20394	59.9	1.37	2.27	1.23
CH_2Cl_2	84.7	198	1.37776	41.6	2.3	4.75	1.49
CCl_3COH	147	220	1.5448	97.2	1.5	2.2	1.33
CCl_4	153.4	271	1.63195	76.7	1.7	3.5	1.56
CCl_3COCl	182	322	1.6564	118	1.76	2.8	1.52
$C(NO_2)Cl_3$	164	326	1.69225	111.9	2	2.9	1.55
CCl_3CHCl_2	202.7	393	1.70893	159.1	1.9	2.47	1.55
CCl_3Br	198	425	2.05496	104.07	2.15	4.07	1.85
C_2H_5ICl	190.5	506	2.161439	140	2.6	3.6	1.88
$C_2H_5Br_2$	188	518	2.21324	131.45	2.8	3.9	1.95
$CHBr_3$	253	646	2.83413	151.2	2.56	4.3	2.16
ICl	162.5	730	3.1822	101.3	4.49	7.2	2.68
$CHCl_3$	119	246	1.52657	61.2	2.07	4.02	1.55
Br_2	160	619	3.18828	60	3.8	10.3	2.68

TABLE II.

Formula.	m.	T.	Specific gravity.	f.	$\frac{T}{m}$	$\frac{T}{f}$	$\frac{T_a}{f_a}$
CS_2	76	112	1.29215	46.04	1.47	2.44	1.21
$PCl_2C_2H_5O$	146.7	210	1.30526	117.5	1.4	1.8	1.24
$SiCl_4$	169.4	244	1.52408	57.57	1.45	4.2	1.5
PCl_5	137	287	1.61275	75.95	2.1	3.78	1.6
$SOCl_2$	118.7	297	1.67673	78.8	2.5	3.77	1.62
$POCl_3$	153	345	1.7116	107.23	2.2	3.2	1.62
$TiCl_4$	189	390	1.76088	136.4	2.06	2.8	1.62
$VOCl_3$	173	440	1.8653	127.19	2.5	3.46	1.78
$POBrCl_2$	197.7	490	2.12065	137.6	2.5	3.6	2.46
AsF_3	132	635	2.6659	60.4	4.8	10.5	2.72
PBr_3	271	792	2.92311	172.9	3.7	4.6	2.39
SO_2Cl_2	135	283	1.70814	69.95	2.1	3.05	1.63
$C_6H_5PCl_2$	178.7	304	1.3428	224.6	1.7	1.36	1.16
$PSCl_3$	169	361	1.6682	125.07	2.1	2.85	1.59
$SSCl_2$	135	402	1.7094	138.12	2.2	2.9	1.64
$SnCl_4$	279	438	2.2787	113.89	1.57	3.8	1.84
CrO_2Cl_2	202.7	494	1.961	115.9	2.4	4.26	1.95
SO_2OHCl	116.5	503	1.78474	155.3	4.3	3.2	1.82

sufficient number of examples had been examined. We should thus have the following conditions:—

Specific gravity $\propto$ temperature of unit specific gravity.
Temperature of unit specific gravity $\propto$ molecular weight
(because $\frac{T}{m}$ approaches constant value), and hence specific gravity $\propto$ molecular weight.

Lastly, there is a greater uniformity between the values of $\frac{T_a}{f_a}$ than between those of $\frac{T}{m}$, and consequently all that has been said with regard to values of $\frac{T}{m}$ applies with even greater force to values of $\frac{T_a}{f_a}$. Moreover, it should

be remarked that the numbers representing $\frac{T_a}{f_a}$, regarded in general, increase with increasing specific gravities, and in fact usually assume values *very closely approximating the actual specific gravities themselves*.

Curve III. represents this relation. Although these curves are represented as straight lines, it will at once be evident that they could, with equal right, be regarded as sinuous, similar to those of Curves I. and II. (Points on Curve I. are expressed by the *multiplication* sign; those on Curve II. by the *addition* sign).

Nothing can be definitely decided until many and more varied liquids have been examined. Consequently this paper can avail nothing except to indicate a possible source of a more intimate connection between the physical properties of liquids.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London January 9th, 1891.

SIR,—We submit herewith the results of our analyses of the 133 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from December 1st to December 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to

oxidise the organic matter in all the samples submitted to analysis.

Of the 133 samples examined, the whole were found to be clear, bright, and well filtered.

It will be noticed that from the 15th to the 31st of the month, the regular examination of samples drawn from the stand-pipes day by day, was largely interfered with by the prevailing frost, which, while considerable also in severity, has not for many years past been equalled in duration, beginning as it did on December 9th, and continuing, practically without intermission, well into the present year. That this wholly exceptional frost, though offering impediments to the process of filtration and retarding the rate of filtration, did not interfere with its thoroughness, is shown by the circumstance that no one sample of water, alike among those included in the Tables, and among numerous supplementary samples submitted to examination, was found otherwise than free from colour and turbidity. Moreover, in respect to chemical characters generally, the water supply for December was found to compare favourably even with the supply of the previous summer and autumn months, as shown in the following Table of results afforded by the water distributed by the Companies taking their supply from the Thames:—

	Ratio of brown to blue tint.	Oxygen required for oxidation.	Organic carbon per 100,000.	Organic carbon per 100,000.
	Means.	Means.	Means.	Maxima.
June	12'0 : 20	0'049	0'150	0'166
July	16'1 : 20	0'056	0'152	0'185
August .. .	17'1 : 20	0'065	0'150	0'175
September ..	11'5 : 20	0'044	0'147	0'170
October .. .	10'4 : 20	0'040	0'136	0'160
November ..	13'1 : 20	0'045	0'142	0'158
December ..	14'8 : 20	0'045	0'136	0'148

It came to our notice, however, that some of the Thames-derived water distributed during the later part of December, and at the commencement of the present year, manifested, in the case of certain particular samples, an unpleasant faint taste associated in yet fewer instances with a corresponding odour. From our analysis of different samples, we were able to satisfy ourselves definitely that the occurrence of this taste and smell, both evanescent, did not depend on any contamination of the water with animal matter; and from a consideration of the exceptional meteorological conditions prevailing of combined frost, fog, and snow, and from our examination of various samples of snow and snow-water, we are inclined to attribute the occurrence in question to an admixture with the main supply of a small proportion of water furnished by the melting of heavily fog-laden snow, such as some of that which we had the opportunity of experimenting on.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

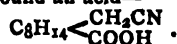
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxii., No. 2, January 12, 1891.

On a Reclamation of Priority on Behalf of M. de Chancourtois with Reference to the Numerical Relations of the Atomic Weights.—MM. Lecoq de Boisbaudran and A. de Lapparent.—Inserted in full.

Action of Sodium Phenol and of Sodium Naphthol upon Camphor Cyanide.—J. Minquin.—The author has formerly shown that sodium benzylate reacting upon camphor cyanide gives rise to a compound—



and that in the washing-waters from the preparation of this body there is found an acid—



Phenol and naphthol behave in a manner absolutely identical.

New Method for Detecting Olive Oil and Seed Oils Equally Applicable to Natural Butters and Oleo-Margarine.—Raoul Brullé.—The reagent employed is a solution of silver nitrate at 25 per 1000 in ethylic alcohol at 95°. About 12 c.c. of the oil in question and 5 c.c. of the reagent are placed in a test-tube. The tube is then set in a beaker of boiling water, and the changes of colour which take place in the liquids are watched through the glass. Unless the oils are perfectly limpid, they must be previously filtered. Olive oils sooner or later take a fine green colour, which is lighter in the superior qualities. Pure cotton-seed oil is turned completely black. Oil of earth nuts (*Arachis*) takes first a red-brown colour and finally turns green, losing its transparency. Oil of sesame takes a deep red colour and remains reddish. Oil of colza takes yellowish green colours and becomes turbid. Natural butter preserves its natural colour. Oleo-margarine becomes a brick-red, which colour may be detected even in samples containing as little as 5 per cent of margarine.

On the Diamond-bearing Sands Collected by C. Rabot in Russian Lapland (Valley of the Pasrig).—Ch. Vélain.—The sands in question contain the following minerals in the order of their frequency:—Garnet (almandine), zircon, amphiboles brown and green, glaucophane, diathene, pyroxene, quartz, corundum, rutile, magnetite, staurolite, andalusite, tourmaline, epidote, felspar (oligoclase), diamond. The diamonds are of the average size of 0'25 m.m.

MISCELLANEOUS.

Researches on Micro-organisms.—His Majesty the King of the Belgians has graciously accepted a copy of Dr. A. B. Griffiths's book, "Researches on Micro-organisms," which has just been published by Messrs. Baillière and Co.

Prix Montyon.—At a meeting of the Académie des Sciences, Paris, held on December 29, Dr. A. B. Griffiths, F.R.S.E., F.C.S., was awarded an "honourable mention" in connection with the Prix Montyon, which is given annually by the Academy for researches in experimental physiology and physiological chemistry.

Preparation of Metallic Manganese by Means of Manganese Chloride and Magnesium.—E. Glatzel.—Crystalline manganese chloride is dehydrated, pulverised, and 100 grms. of the mass are mixed with 200 grms. of potassium chloride in fine powder and perfectly dry. The whole is placed in a Hessian crucible, covered with its lid, and heated to near redness. When the mass is in quiet fusion 15 grms. of magnesium, broken up into fragments of 3—4 grms., are added in four or five portions. When the reaction is over the crucible is covered, and the heat is raised to the strongest redness. When cold a metallic regulus of 20—25 grms. is found at the bottom of the crucible. The metal thus obtained is harder than a steel file. It is not at all attracted by a powerful magnet. It is permanent in dry air, but rusts readily in moist air and is easily attacked by acids. It contains mere traces of magnesium.—*Journal de Pharm. et de Chimie*, Vol. xxii., No. 1.

The Chemical Society's Jubilee, 1897. — The Chemical Society, having been founded in 1847, is in the fiftieth year of its existence, and is the eldest among chemical societies. The following arrangements have been made to celebrate this important occurrence in the history of the Society on February 24th and 25th next:—On February 24th, at 3—5 o'clock p.m., a Meeting will be held at the Society of Arts, where the original meeting took place at which the formation of the Society was decided on. At this meeting various addresses will be delivered, and delegates from other Societies will be received. On the evening of the same day, at 8.30 o'clock, the President and Council will hold a Reception at the Goldsmiths' Hall, which has been most kindly placed at the disposal of the Society for the purpose by the Worshipful Company of Goldsmiths. On the evening of February 25, at 6.30 for 7 p.m., the Fellows and their friends will dine together at the Hotel Métropole. (Tickets one guinea each).

MEETINGS FOR THE WEEK.

- MONDAY, 2nd.**—Medical, 8.30.
— Society of Chemical Industry, 8. "On Standard Sperm Candles," by W. C. Young.
— Society of Arts, 8. "The Construction and Capabilities of Musical Instruments," by A. J. Hipkins, F.S.A.
— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 3rd.—Institute of Civil Engineers, 8.
— Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley, F.R.S., B.S., F.R.C.S., Fullerian Professor of Physiology, R.I.
— Pathological, 8.30.
WEDNESDAY, 4th.—Society of Arts, 8. "Decimal Coinage, Weights, and Measures," by J. Emerson Dowson.
— Geological, 8.
THURSDAY, 5th.—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "The Little Manx Nation," by Hall Caine.
— Chemical, 5.
FRIDAY, 6th.—Royal Institution, 9. "Some Applications of Photography," by The Right Hon. Lord Rayleigh, F.R.S.
— Geologists' Association, 7.30. (Anniversary).
— Quekett, 8.
SATURDAY, 7th.—Royal Institution, 3. "Pre-Greek Schools of Art," by W. Martin Conway, M.A., F.S.A.

TO CORRESPONDENTS.

C. O'N. Williams.—Dr. Letheby died March 28, 1876.

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THE CHEMICAL NEWS.

VOL. LXIII., No. 1628.

ON GASEOUS ILLUMINANTS.*

By Professor VIVIAN B. LEWES.

V.

It has been proposed to carburet and enrich poor coal gas by admixture with it of an oxy-oil gas, in which crude oils are cracked at a comparatively low temperature, and are then mixed with from 12 to 24 per cent of oxygen gas. Oil gas made at low temperature is *per se* of little use as an illuminant, as it burns with a smoky flame and does not travel well; but when mixed with a certain amount of oxygen it gives a very brilliant white light and no smoke, while, as far as experiments have at present gone, its travelling powers are much improved. At first sight it seems a dangerous experiment to mix a heavy hydrocarbon gas with oxygen; but it must be remembered that although hydrogen and carbon monoxide only need to be mixed with but half of their own volume of oxygen to produce the most explosive compound, yet as the number of carbon and hydrogen atoms in the combustible gas increases, so does the amount of oxygen needed. So that coal gas requires rather more than its own volume, and ethylene three times its volume, to yield the maximum explosive results; while these mixtures begin to be explosive when 10 per cent of oxygen is combined with hydrogen or water gas, 30 per cent with coal gas, and more than 50 per cent with oil gas of the character used. It is claimed that if this gas were used as an enricher of coal gas, 5 per cent of it would increase the luminosity of 16-candle gas by about 40 per cent. Oxygen has been obtained for some time past from the air, on a commercial scale, by the Brin process; and it is now proposed to make oxygen by a process first introduced by Tessié du Motay, which consists of passing alternate currents of steam and air over sodic manganate heated to dull redness in an iron tube. The process has never been commercially successful, for the reason that the contents of the tube fused, and, flowing over the surface of the iron, rapidly destroyed the tubes or retorts; and also, as soon as fusion took place, the mass became so dense that it had little or no action on the air passing over it, but it is now claimed that this trouble can be overcome. Cheap oxygen would be an enormous boon to the gas manager, as, by mixing 10·8 per cent of oxygen with his coal gas before purification, he could not only utilise the method so successfully introduced by Mr. Valon at Ramsgate, but could also increase the illuminating value of his gas to a slight extent.

No ordinary gas flame is in contact with the burner from which it issues, this being due to the cooling effect of the burner, but as this only affects the bottom of the flame, with a small flame the total effect is very great, with a large flame almost nil. The first point, therefore, to attend to, is that the burner should be made of a good non-conductor. In the next place, the flow of the gas must be regulated to the burner; as, if you have a pressure higher than that for which the burner is constructed, you at once obtain a roaring flame and a loss of illuminating power, as the too-rapid rush of gas from the burner causes a mingling of gas and air, and a consequent cooling of the flame, while the form of the flame becomes distorted. The tap also which regulates the flame is better at a distance from the burner than close to it, as any constriction near the burner causes eddies in the flow of the gas, which gives an unsteady flame. These general principles govern all burners.

* Abstract of the Cantor Lectures delivered at the Society of Arts. Communicated by the Author.

We will now take the ordinary forms in detail. In the flat-flame burner, given a good non-conducting material and a well-regulated gas supply, little more can be done, while burning it in the ordinary way, to increase its luminosity; and it is the large surface of flame exposed to the cooling action of the air which causes this form of burner to give the lowest service of any per cubic foot of gas consumed. Much is done, moreover, by faulty fittings and shades, to reduce the already poor light afforded, because the light-yielding power of the flame largely depends on its having a well-rounded base and broad luminous zone; and when a globe with narrow opening is used with such a flame as is done in ninety-nine cases out of a hundred, the up-draught drags the flame out of shape, and seriously impairs its illuminating power—a trouble which can be overcome by having a globe with an opening at the bottom not less than 4 inches in diameter, and having small shoulders fixed to the burner which draw out the flame and protect the base from the disturbing influence of draughts.

The Argand burner differs from the flat-flame burner in that a circular flame is employed, and the air supply is regulated by a glass of cylindrical form. This kind of burner gives better service than a flat-flame, as not only can the supply of gas and air be better adjusted, but the air being slightly warmed by the hot glass, adds to the temperature of the flame, which is also increased by radiation from the opposite side of the flame itself. The chief loss of light depends upon the fact that, being circular, the light from the inner surface has to pass through the wall of flame; and careful photometric experiments show that the solid particles present in the flame so reduce its transparency that a loss amounting to about 25 per cent of light takes place during its transmission.

For many years no advance was made upon these forms of burner. But when, fifteen years ago, it was recognised that anything which cools the flame reduces its value, while anything which increases its temperature raises its illuminating power, a change began to steal over the forms of burner in use; and the regenerative burners, fathered by such men as Siemens, Grimsen, and Bower, commenced what was really a revolution in gas lighting, by utilising the heat contained in the escaping products of combustion to raise the temperature of the gas and air which are to enter into combination in the flame. An enormous increase in the temperature of the solid particles of carbon in the flame is thereby obtained, and a far greater and whiter light is the result.

The only drawback to this class of burner is that it is by far the best form of gas stove as well as burner, and that the amount of heat thrown out by the radiant solid matter in the flame is, under some circumstances, an annoyance. On the other hand, we must not forget that this is the form of burner best adapted for overhead lighting, and that nearly every form of regenerative lamp can be used as a ventilating agent; and that with the withdrawal of the products of combustion from the air of the room, the great and only serious objection to gas as an illuminant disappears.

When coal gas is burnt, the hydrogen is supposed to be entirely converted into water vapour, and the carbon to finally escape into the air as carbon dioxide. If this were so, every cubic foot of gas consumed would produce approximately 0·523 cubic foot of carbon dioxide, and 1·34 cubic feet of water vapour, and the illuminating power yielded by the foot of gas will, of course, vary with the kind of burner used.

Roughly speaking, the ordinary types of burner give the following results:—

	Illuminating Power in candles per c. ft. of gas consumed.	Products of combustion per candle power.	
		Carbon dioxide.	Water vapour.
Batwing ..	2·9	0·18 c. ft.	0·46 c. ft.
Argand ..	3·3	0·16 "	0·40 "
Regenerative ..	10·0	0·05 "	0·13 "

So that the regenerative forms of burner, by giving the greatest illuminating power per cubic foot of gas consumed, yield a smaller amount of vitiation to the air per candle of light emitted. An ordinary room (say, 16 ft. by 12 ft. by 10 ft.), would not be considered properly illuminated unless the light were at least equal to 32-candle power; and in the following table the amount of oxygen used up, and the products of combustion formed by each class of illuminant and burner, in attaining this result, are given. The number of adults who would exhale the same amount during respiration is also stated:—

Illuminants.	Quantity of materials used.	Products of Combustion.				Adults.
		Oxygen removed.				
			Water vapour.	Carbon dioxide.		
	Grms.	C. ft.	C. ft.	C. ft.		
Sperm candles ..	3840	19'27	13'12	13'12	21'8	
Paraffin oil ..	1984	12'48	7'04	8'96	14'9	
Gas (London)—		C. ft.	C. ft.	C. ft.		
Batawing burner.	11'0	13'06	14'72	5'76	9'6	
Argand „ ..	9'7	11'52	12'80	5'12	8'5	
Regenerative ..	3'2	3'68	4'16	16'0	2'6	

From these data it appears, according to scientific rules by which the degree of vitiation of the air in any confined space is measured by the amount of oxygen used up and carbon dioxide formed, that candles are the worst offenders against health and comfort; oil lamps come next, and gas least. This, however, is an assumption which practical experience does not bear out. Discomfort and oppression in a room lighted by candles or oil are less felt than in one lighted by any of the older forms of gas-burner. The partial explanation of this is to be found in the fact that, when a room is illuminated with candles or oil, people are contented with a feebler and more local light than when using gas. In a room of the size described, the inmates would be more likely to use two candles placed near their books, or on a table, than 32 candles scattered about the room. Moreover, the amount of water vapour given off during the combustion of the gas is greater than in the case of the other illuminants. Water vapour, having a great power of absorbing radiant heat from the burning gas, becomes heated; and, diffusing itself about the room, causes a great feeling of oppression. The air also, being highly charged with moisture, is unable to take up so rapidly the water vapour which is always evaporating from the surface of the skin, whereby the functions of the body receive a slight check, resulting in a feeling of *malaise*. Added to these, however, is a far more serious factor, which up to the present has been overlooked, and that is that an ordinary gas-flame in burning yields distinct quantities of carbon monoxide and acetylene, the prolonged breathing of which, in the smallest traces, produce headache and general physical discomfort, while their effect upon plant life is equally marked.

Ever since the structure of flame has been noted and discussed, it has been accepted as a fact beyond dispute that the outer, almost invisible zone which is interposed between the air and the luminous zone of the flame is the area of complete combustion; and that here the unburnt remnants of the flame gases, meeting the air, freely take up oxygen, and are converted into the comparatively harmless products of combustion, carbon dioxide and water vapour, which only need partial removal by any haphazard process of ventilation to keep the air of the room fit to support animal life. I have, however, long doubted this fact; and at length, by a delicate process of analysis, have been able to confirm my suspicions. The outer zone of the luminous flame is not the zone of complete combustion. It is a zone in which luminosity is destroyed in exactly the same way that it is destroyed in the Bunsen burner—i.e., the air penetrating the flame so dilutes and cools down the outer layer of incandescent gas, that it is rendered non-luminous; while some of the gas sinks below the point at which it is capable of burning, with the result that considerable quantities of the

products of incomplete combustion (carbon monoxide and acetylene) escape into the air, and render it actively injurious. I have proved this by taking a small platinum pipe with a circular loop at the end—the interior of the loop being pierced with minute holes; and by making a circular flame burn within the loop, so that the non-luminous zone of the flame just touched the inside of the loop, and then by aspiration, so gentle as not to distort the shape of the flame, withdrawing the gases escaping from the outer zone, and analysing these by a delicate process which will be described elsewhere, I arrived at the following results:—

Gases Escaping from the Outer Zone of Flame.

	Luminous.		Bunsen.	
	100'000	100'000	100'000	100'000
Nitrogen ..	76'612	..	80'242	..
Water vapour ..	14'702	..	13'345	..
Carbon dioxide ..	2'201	..	4'966	..
Carbon monoxide ..	1'189	..	0'006	..
Oxygen ..	2'300	..	1'430	..
Marsh gas ..	0'072	..	0'003	..
Hydrogen ..	2'388	..	0'008	..
Acetylene ..	0'036	..	nil	..

The gases leaving the luminous flame show that the diluting action of the nitrogen is so great that considerable quantities even of the highly-inflammable and rapidly-burning hydrogen escape combustion; while the products of incomplete combustion are present in sufficient quantity to perfectly account for the deleterious effects of gas-burners in ill-ventilated rooms. The analyses also bring out very clearly the fact that, although the dilution of coal gas by air in atmospheric burners is sufficient to prevent the decomposition of the heavy hydrocarbons, with liberation of carbon, and so destroy luminosity, yet the presence of the extra supply of oxygen does make the combustion far more perfect, so that the products of incomplete combustion are hardly to be found in the escaping gases.

The feeling has gradually been gaining ground in the public mind that, when atmospheric burners and other devices for consuming coal gas are employed for heating purposes, certain deleterious products of incomplete combustion find their way into the air; and that this does take place to a considerable extent is shown by the facts brought forward in a paper read by Mr. W. Thompson at the last meeting of the British Association, at Leeds (CHEM. NEWS, lxii., p. 193). Mr. Thompson attempted to separate and determine the quantity of carbon monoxide and hydrocarbons found in the flue gases from various forms of gas stoves and burners; but, like every other observer who has tried to solve this most difficult problem, he found it so beset with difficulties that he had to abandon it, and contented himself with determining the total quantities of carbon and hydrogen escaping in an unburnt condition. His experiments proved that the combustion of gas in stoves for heating purposes is much more incomplete than one had been in the habit of supposing; but they did not show whether the incompletely burnt matter consisted of such deleterious products as carbon monoxide and acetylene, or comparatively harmless gases such as marsh gas and hydrogen.

If a cold substance—metallic or non-metallic—be placed in a flame, whether it be luminous or non-luminous, it will be observed that there is a clear space, in which no combustion is taking place, formed round the cool surface, and that, as the body is heated, this space becomes gradually less, until, when the substance is at the same temperature as the flame itself, there is contact between the two. Moreover, when a luminous flame is employed in this experiment, the space still exists between the cool body and the flame; but it will also be noticed that the luminosity is decreased over a still larger area, though the flame exists. This means that in immediate contact with the cool body the temperature is so reduced that a flame

cannot exist, and so is extinguished over a small area; while over a still larger space the temperature is so reduced that it is not hot enough to bring about decomposition of the heavy hydrocarbons, with liberation of carbon, to the same extent as in hotter portions of the flame.

Now, inasmuch as when water is heated or boiled in an open vessel, the temperature cannot rise above 100° C., and as the temperature of an ordinary flame is more than 1000° C., it is evident that the burning gas can never be in contact with the bottom of the vessel; or, in other words, the gas is put out before combustion is completed, and the unburnt gas and products of incomplete combustion find their way into the air, and render it perfectly unfit for respiration. The portion of the flame which is supposed to be the hottest is about half an inch above the tip of the inner zone of the flame. It is at this point that most vessels containing water to be heated are made to impinge on the flame; and it is this portion of the flame also that is utilised for raising various solids to a temperature at which they will radiate heat in most forms of gas-stove.

I have determined the composition of the products of combustion and the unburnt gases escaping when a vessel containing water at the ordinary temperature is heated up to boiling-point by a gas flame; the vessel being placed in the first case half an inch above the inner cone of the flame, and in the second at the extreme outer tip of the flame. The results are given in the following table:—

Gases Escaping during Checked Combustion.

	Bunsen flame.		Luminous flame.	
	Inner.	Outer.	Inner.	Outer.
Nitrogen	75.75	79.17	77.52	69.41
Water vapour ..	13.47	14.29	11.80	19.24
Carbon dioxide ..	2.99	5.13	4.93	2.38
Carbon monoxide	3.69	nil	2.45	2.58
Marsh gas	0.51	0.31	0.95	0.39
Acetylene	0.04	nil	0.27	nil
Hydrogen	3.55	0.47	2.08	nil
	100.00	100.00	100.00	100.00

These figures are of the greatest interest, as they show conclusively that the extreme tip of the Bunsen flame is the only portion which can be used for heating a solid substance without liberating deleterious gases. This corroborates the previous experiment on the gases in the outer zone of the flame, which showed that the outer zone of the Bunsen flame is the only place where complete combustion is approached. Moreover, this work sets at rest a question which has been over and over again under discussion, and that is whether it is better to use a luminous or a non-luminous flame for heating purposes. Using a luminous flame, it is impossible to prevent a deposit of carbon, which is kept by the flame at a red heat on its outer surface; and the carbon dioxide formed by the complete combustion of the carbon already burnt up in the flame is by this reduced back to carbon monoxide. So that, even in the extreme tip of a luminous flame, it is impossible to heat a cool body without giving rise to carbon monoxide, although, acetylene being absent, gas-stoves in which small flat flame burners are used have not that subtle and penetrating odour which marks the ordinary atmospheric burner stove with the combustion checked just at the right spot for the formation of the greatest volume of noxious products. It is the contact of the body to be heated with the flame before combustion is complete that gives rise to the great mischief. Any cooling of the flame extinguishes a portion of it; and the gases present in it at the moment of extinction creep along the cooled surface, and escape combustion.

In utilising a flame for heating purposes combustion must be completed before any attempt is made to use the heat; in other words, the products of combustion and not the flame must be used for this purpose.

I think I have said enough to show that no geyser or

gas-stove should be used without ample and thorough means of ventilation being provided; and no trace of the products of combustion should be allowed to escape into the air. Until this is done, the use of improper forms of stoves will continue to inflict serious injury on the health of the people using them; and this will gradually result in the abandonment of gas as a fuel, instead of, as should be the case, its coming into general use.

Let us now consider for a moment what is likely to be the future of gas during the next half-century. The labour troubles, bad as they are and have been, will not cease for many a weary year. The victim of imperfect education—more dangerous than none at all, as, while destroying natural instinct, it leaves nothing in its place—will still listen to, and be led by the baneful influence of irresponsible demagogues, who care for nothing so long as they can read their own inflammatory utterances in the local press, and gain a temporary notoriety at the expense of the poor fools whose cause they profess to serve. The natural outcome of this will be that every possible labour-saving contrivance will be pressed into the gas manager's service, and that although coal (of a poorer class than that now used) will still be employed as the source of gas, the present retort-setting will quickly give way to the inclined retorts on the Coze principle; while instead of the present wasteful method of quenching the red hot coke, it will, as far as it can be used, be shot direct into the generator of the water-gas plant, and the water-gas, carburetted with the benzene hydrocarbons derived from the smoke of the blast furnaces and coke ovens, or from the creosote oil of the tar distiller, by the process foreshadowed in the concluding sentences of the preceding lecture, will then be mixed with the gas from the retorts, and will supply a far higher illuminant than we at present possess. In parts of the United Kingdom, such as South Wales, where gas-coal is dear and anthracite and bastard coals are cheap, water gas, highly carburetted, will entirely supplant coal gas, with a saving of 50 per cent on the prices now existing in these districts.

While these changes have been going on, and improved methods of manufacture have been tending to the cheapening of gas, it will have been steadily growing in public favour as a fuel; and if, in years to come, the generation of electricity should have been so cheapened as to allow the electric light to successfully compete with gas as an illuminant, the gas works will still be found as busy as of yore, and the holder of gas shares as contented as he is to-day; for, with the desire for a purer atmosphere and white mist instead of yellow fog, gas will have largely supplanted coal as a fuel, and gas stoves, properly ventilated and free from the reproaches I have hurled at them to-night, will burn a gas far higher in its heating power than that we now use, far better as regards its capacity for bearing illuminating hydrocarbons, and entirely free from poisonous constituents. As soon as the demand for it arises, hydrogen gas can be made as cheaply as water gas itself; and when the time is ripe for a fuel gas for use in the house, it is hydrogen and not water gas that will form its basis. With carburetted water gas and 20 per cent of carbon monoxide, we shall still be below the limit of danger; but a pure water gas, with more than 40 per cent of the same insidious element of danger, will never be tolerated in our households. Already a patent has been taken by Messrs. Crookes and Ricarde-Seaver for purifying water gas from carbon monoxide, and converting it mainly into hydrogen by passing it at a high temperature through a mixture of lime and soda-lime—a process which is chemically perfect, as the most expensive portion of the material used could be recovered.

From the earliest days of gas making, the manufacture of hydrogen by the passage of steam over red hot iron has been over and over again mooted and attempted on a large scale; but several factors have combined to render it futile. In the first place, for every 478.5 cubic feet of hydrogen made under perfect theoretical conditions never likely to be obtained in practice, 56 lbs. of

iron were converted into the magnetic oxide; and as there was no ready sale for this article, this alone would prevent it being used as a cheap source of hydrogen. The next point was that, when steam was passed over the red hot iron, the temperature was so rapidly lowered that the generation of gas could only go on for a very short period. Finally, the swelling of the mass in the retort, and the fusion of some of the magnetic oxide into the side, renders the removal of the spent material almost an impossibility. These difficulties can, however, be overcome. Take a fire-clay retort 6 feet long and 1 foot in diameter, and cap it with a casting bearing two outlet tubes closed by screw valves, while a similar tube leads from the bottom of the retort. Enclose this retort, set on end, by a furnace chamber of iron, lined with fire brick, leaving a space of 2 ft. 6 in. round the retort; and connect the top of the furnace chamber with one opening at the top of the upright retort, while an air blast is led into the bottom of the furnace chamber below rocking fire bars, which start at the bottom of the retort, and slope upwards to leave room for ash holes closed by gas-tight covers. The retort is filled with iron or steel borings—alone if pure hydrogen is required, or cast into balls with pitch if a little carbon monoxide is not a drawback, as in foundry work. The furnace chamber is filled with coke, fed in through manholes or hoppers in the top; and the fuel being ignited, the blast is turned on, and the mixture of nitrogen and carbon monoxide formed passes over the iron, heating it to a red heat, while the incandescent coke in contact with the retort does the same thing. When the fuel and retort full of iron are at a cherry-red heat, the air-blast is cut off, and the pipe connecting the furnace and retort, together with the pipe in connection with the bottom of the retort, is closed. Steam, superheated by passing through a pipe led round the retort or interior wall of the furnace, is injected at the bottom of the red hot mass of iron, which decomposes it, forming magnetic oxide of iron and hydrogen, which escape by the second tube at the top of the retort, and are led away—to a carburetting chamber if required for illumination, or else direct to the gas-holder if wanted as a fuel; the mass of incandescent fuel in the furnace chamber surrounding the retort keeping up the temperature of the retort and iron sufficiently long to enable the decomposition to be completed. The hydrogen and steam valves are now closed, and the air-blast turned on; and the hot carbon monoxide, passing over the hot magnetic oxide, quickly reduces it down again to metallic iron, which, being in a spongy condition, acts more freely on the steam during later makes than it did at first, and, being infusible at the temperature employed, may be used for a practically unlimited period. What more simple method than this could be desired? Here we have the formation of the most valuable of all fuel gases at the cost of the coke and steam used—a gas also which has double the carrying power for hydrocarbon vapours possessed by coal gas, while its combustion gives rise to nothing but water vapour.

A NEW SOLVENT FOR CELLULOSE.

By C. F. CROSS and E. J. BEVAN.

HITHERTO we have had no acid solvent for cellulose, but such as in dissolving it bring about marked changes in composition and properties; in dissolving, the cellulose is resolved, *e.g.*, by the action of sulphuric and phosphoric acids, into products of lower molecular weight, and cannot be recovered from the solution. Concentrated hydrochloric acid, as is well known, attacks cellulose profoundly; when digested with the acid in the cold the fibres are completely disintegrated, and the resulting modification, obtained as a white powder, manifests very different properties from the original. When warmed with aqueous solutions of the alkalis it is coloured deep yellow, and the

products of hydrolysis are powerful reducing agents (aldehyds). Some of the OH groups are also so affected that they react with acetic anhydride at its boiling temperature, giving, so far as our determinations show, the diacetate of a C_{18} compound. We find, however, that on dissolving in the acid one-half its weight of zinc chloride, a solution is obtained (of specific gravity 1.44), which dissolves cellulose instantly and without sensible modification. This observation is of importance, as it enables us to investigate some points in the constitution of cellulose, for the determination of which such an acid solution is an essential condition. The solution of cellulose obtained by heating it with concentrated solutions of zinc chloride may also be diluted with hydrochloric acid without precipitating the dissolved products; but the solution by the new reagent has the double advantage of being instantaneous, and of being prepared, therefore, with the minimum of resolution of the cellulose into bodies of lower molecular weight which usually attends the somewhat prolonged heating necessary for complete solution in the aqueous solution of zinc chloride.

The reagent we also find of great value in the investigation of structural points, *i.e.*, as an aid to microscopic work in the province of the vegetable fibres. All forms of pure cellulose are rapidly dissolved by the reagent, and the various stages preceding their final disappearance may be observed under the microscope, the observation throwing much light on structural peculiarities. The raw fibres, *e.g.*, cotton and flax, are not dissolved; at least, only partially, but swell up under the action of the reagent, with the result that the structural features are brought out with great prominence. Jute and the ligno-celluloses generally are dissolved by the reagent, and many of the adipo-celluloses also. We are investigating these actions more closely, and hope shortly to publish an account of our observations. In the meantime, we commend the reagent in question to all who are engaged in the chemical or microscopic investigation of the vegetable fibres.

VOLUMETRIC ESTIMATION OF MANGANESE.

By THOMAS MOORE.

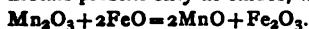
THE present volumetric methods for the estimation of manganese involve so many not easily obtainable conditions that, in the great majority of cases, the gravimetric methods appear to be the only ones employed, and indeed this is not to be wondered at, as during the time spent in procuring the manganese in a suitable condition for titrating, an expert analyst would probably have finished the analysis gravimetrically. The process given below will, I hope, be found to be a decided advance both as regards time and accuracy, and trust it may be of some service to those especially who are often placed in the position to estimate rapidly and accurately the total amount of manganese in slags, &c.

The process depends for its principle on the conversion of the manganese into the fine violet-coloured manganic metaphosphate, MnP_3O_9 , and the titration of this compound by some reducing agent, such as ferrous sulphate, *i.e.*, until the violet colour completely disappears, thus indicating the complete reduction to manganous metaphosphate and end of the reaction.

For the oxidation of the manganese to the manganic state, I have found potassic chlorate to be the most effective and convenient; nitric acid also gives a complete oxidation, but the formation of nitrites at a later stage of the process exercises a reducing effect, and gives results considerably below the truth.

The substance to be examined is dissolved in a suitable solvent, and the solution concentrated until only 2 or 3 c.c. remain; then add 10 to 20 c.c. syrupy phosphoric acid, or the substance may (as is not unfrequently the case), be dissolved directly in the phosphoric acid. The acid

most suitable for the above purpose is that known as syrupy phosphoric acid, having a specific gravity of about 1.75. A few crystals of potassic chlorate are now added to the mixture, and the whole gently warmed until the action, at first rather energetic, becomes quieter; the heat may now be increased and the solution left to itself until all odour of chlorine has vanished. The addition of the potassic chlorate causes the liquid to become of a dirty pink colour; this, however, on the continued application of heat, gradually changes to a magnificent deep violet, strongly resembling that of a solution of potassic permanganate. The thick syrupy liquid after cooling is then dissolved in about 100 c.c. water, and titrated directly by means of a solution of ferrous sulphate, continuing the addition of the latter until the violet colour is dissipated, or add at once a known quantity of the iron solution, and titrate back the excess by means of potassic permanganate in the usual manner. Having found by either method the amount of iron oxidised, a simple calculation will give the quantity of manganese present. Thus, considering the metals present only as oxides, we have—



Hence, 1 part of Fe represents 1.4108 parts Mn_2O_3 .

Everything considered, the best reducing agent is probably the ferrous sulphate, as it may be prepared when required from metallic iron, besides giving a sharper and more decided reaction than oxalic acid, &c.

In testing this method with such compounds as the sulphate, the carbonate, or the pyrophosphate of manganese, the results obtained were excellent, and in the analysis of some minerals, slugs, &c., the figures found agreed so well with those by the gravimetric method that it would be difficult to decide in which process the error lay.

As far as my experience has gone, the only metal which interferes is chromium; this being oxidised by the potassic chlorate, passes into solution, and, oxidising the iron, gives a false number. Cobalt, which under the circumstances might be supposed to pass into a higher state of oxidation, does not interfere, provided care is taken that all free chlorine is expelled before proceeding to titrate; nevertheless, appearances seem to indicate the formation of a somewhat similar compound at lower temperatures, the liquid assuming a deep brown colour. Inasmuch as the rose colour of the cobalt marks the end of the decomposition, it is best first to add an excess of the iron solution, then, after neutralising the cobalt colouration by the addition of sufficient nickelous sulphate, titrate back the excess of iron by permanganate of potassium.

In conclusion it may be observed that phosphoric acid is a powerful solvent for certain silicates, and even glass is strongly attacked when the temperature is raised sufficiently.

This, New Caledonia,
December 1, 1890.

THE ACTION OF THE SILENT DISCHARGE OF ELECTRICITY ON CHLORINE.

By H. M. VERNON.

Arguing from the fact that oxygen gas, when subjected to the silent discharge of electricity, partially undergoes condensation into ozone, it seemed possible that other elementary gases, as chlorine and bromine vapour, might undergo an analogous change when subjected to the same treatment. Accordingly, a glass tube, with a U-shaped index of fine-bore glass tubing, similar to those used by Andrews and Tait in their experiments on ozone (*Phil. Trans.* 1860, 113), was filled with purified and dried chlorine. After passing a current of the gas through the tube for some time, the end was sealed in the blowpipe flame. The tube was then warmed slightly, and a few

bubbles of gas thus driven out. The end of the index tube dipped under strong sulphuric acid saturated with chlorine gas, so that, on cooling, a short column of the acid was drawn up. This served as an index for any changes of volume which might take place in the chlorine in the tube.

A silent discharge of electricity from a large induction coil connected with four Grove's cells was then passed between the platinum wires sealed in the tube. The volume of the gas was soon observed to increase slightly, but after this the volume remained quite constant even after the discharge had been passed for several hours. The discharge from a single cell and a smaller induction coil produced the same effect, except that the initial increase of volume was not quite so large. We may therefore conclude that no allotropic change takes place when chlorine gas is subjected to the silent discharge of electricity, the initial increase of volume being merely due to the heating effect the discharge has upon the gas.

Into another similar tube, filled with chlorine, was introduced a small quantity of liquid bromine. The tube thus contained chlorine saturated with bromine vapour. The silent discharge, on being passed through this tube, did not produce any different effect than for chlorine alone, so we may conclude that bromine vapour also does not undergo any allotropic condensation when subjected to the influence of a silent discharge of electricity. If a contraction of volume had taken place, it would have been necessary to have made experiments with bromine vapour unmixed with chlorine; for such a contraction might be due to the formation or condensation of a chloride of bromine. The fact of no contraction taking place proves, however, that the bromine underwent no change. If bromine vapour alone were used, it would have been necessary to heat the tube to above the boiling-point of bromine before passing the discharge, and as it would be difficult to keep the temperature so constant as at ordinary temperatures, the experiment was not made.

The fact that oxygen gas is capable of undergoing condensation while chlorine and bromine are not, is easily explained. The oxygen atom being divalent is capable of uniting itself to two other atoms of oxygen or other elements, and thus with oxygen forming ozone



The atoms of chlorine and bromine, however, being only monovalent, have all their affinity satisfied when they are united to a single other atom of chlorine and bromine, thus, Cl—Cl, Br—Br. It is not possible, therefore, that condensation can take place if the atoms remain monovalent. Hydrogen gas and iodine vapour are in a similar manner debarred from undergoing condensation.

The atoms of nitrogen being trivalent are theoretically capable of undergoing condensation and forming molecules with four or more atoms, thus—



They cannot, however, condense to molecules with three atoms without the existence of free affinities. Looking at the great stability of the nitrogen molecule, and the instability of the ozone molecule, which contains only three atoms of oxygen, it does not seem probable that such a modification is capable of existing. The possibility of such a condensation taking place is, however, proved by the existence of the similarly constituted molecules of phosphorus and arsenic vapours.

The hexatomic molecules of sulphur and selenium, known to exist at temperatures not far removed from the boiling-points of these elements, are another example of the condensation of polyvalent atoms when situated under suitable conditions. Inasmuch as these molecules are dissociated into diatomic molecules at higher temperatures, it would not be possible to re-form them by the

action of the silent discharge upon the diatomic molecules. The very slight affinity that atoms of metallic elements have for each other when in the state of vapour is too well-known to need comment. We therefore come to the conclusion that it is not probable that any other elements but oxygen will be found capable of undergoing molecular condensation when, in the gaseous state, subjected to the silent discharge of electricity.

**ELECTRICITY
IN TRANSITU :
FROM PLENUM TO VACUUM.***

By WILLIAM CROOKES, F.R.S.,
President of the Institution of Electrical Engineers.

(Continued from p. 56).

The Dark Space.

AFTER the stratification stage is passed we come to a very curious phenomenon, the so-called "Dark Space." Studying electrical phenomena in gases, in the year 1838, Faraday† pointed out a break in the continuity of the luminous discharge separating the glow of the positive

slightly rarefied, as in this tube (Fig. 5, P.=6 m.m.), where you will observe that the positive glow, extending as a pink streak from the positive electrode, B, ends about ten millimetres before the spot of blue light, c, representing the negative glow. This gap, or non-luminous hiatus, D, is Faraday's "dark space." Separating the negative glow from its electrode is another space. In this tube it is so small that the glow appears to be in actual contact with the electrode, but on exhausting a little further it rapidly separates; and in the next tube (Fig. 6), containing air at a little less pressure (P.=3 m.m.), this dark space, E, has extended so as to remove the negative glow about four millimetres from the electrode, A. It is with this second dark space that I particularly wish to deal to-night. Therefore I shall refer to it as the "dark space," meaning always that in the negative glow.

In the experiments just shown with hydrogen stratifications the contents of the tube under the electric discharge still obey the laws following from the average properties of an immense number of molecules moving in every direction with velocities of all conceivable magnitudes. But if I continue exhausting, the dark space, E, round the negative pole, A, becomes visible, grows larger and larger, and at last fills up the entire tube. The molecules at this stage are in a condition different from those in a less highly exhausted tube. At low exhaustions they behave

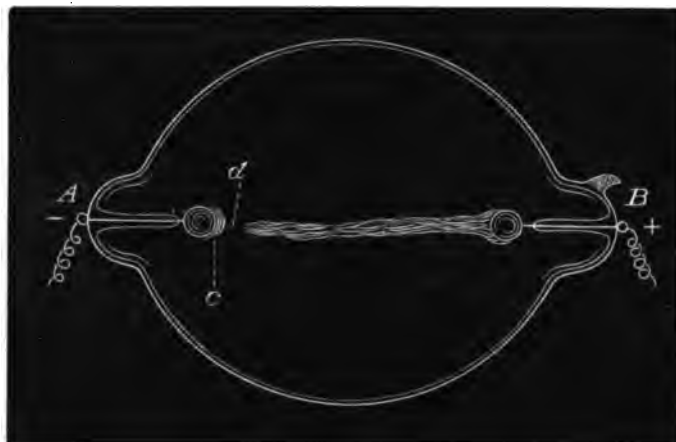


FIG. 5.—P. = 6 m.m.

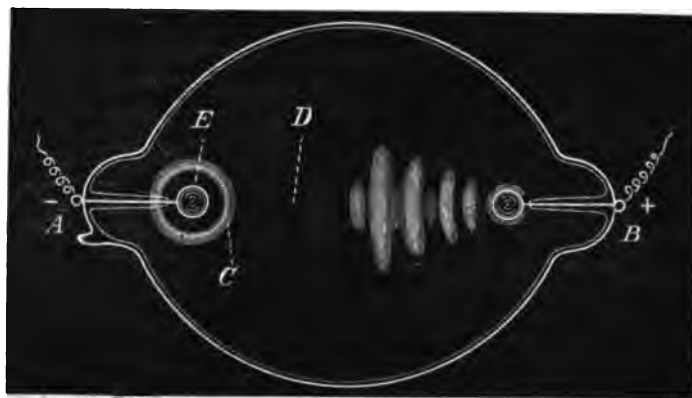


FIG. 6.—P. = 3 m.m.

electrode from that of the negative. This he called "the dark space." It is seen in tubes containing gas only

* Inaugural Address delivered January 15th, 1891.

† "Experimental Researches in Electricity," 1838, par. 1544.

as gas in the ordinary sense of the term, but at these high exhaustions, under electric stress, they have become exalted to an *ultra-gaseous* state, in which very decided properties, hitherto masked, come into play.

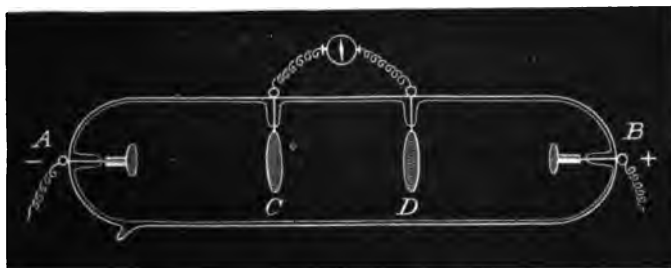


FIG. 7.

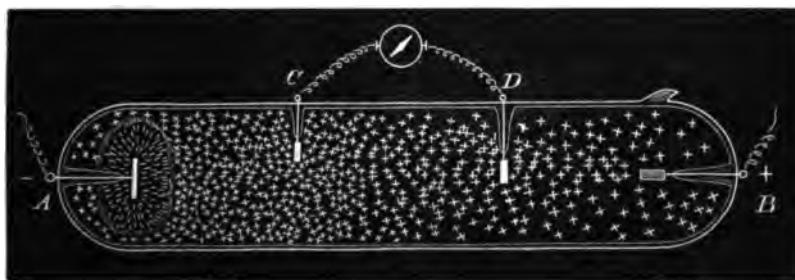


FIG. 8a.—P. = 0.25 m.m.

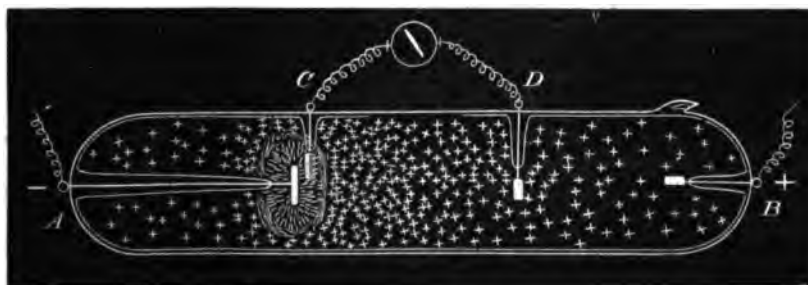


FIG. 8b.—P. = 0.25 m.m.

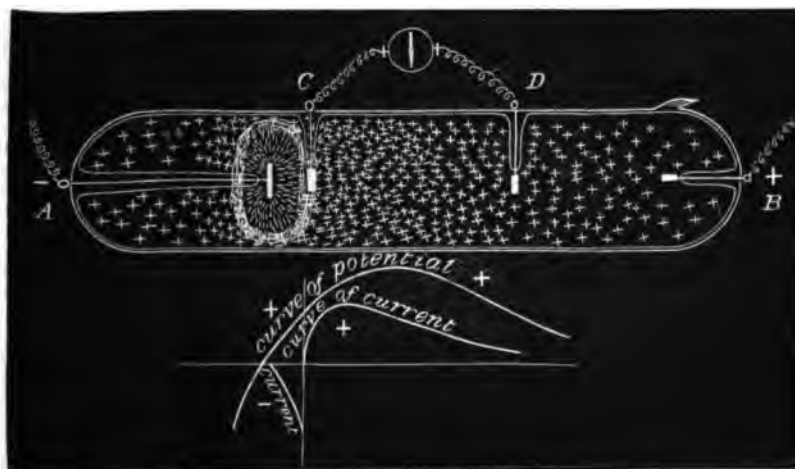


FIG. 8c.—P. = 0.25 m.m.

The radius of the dark space varies with the degree of exhaustion, with the kind of gas in which it has been produced, with the temperature of the negative pole, and to a less extent with the intensity of the spark.

It has been erroneously assumed that I ever said the thickness of the "dark space" represents the mean free path of the molecules in their ordinary condition, and it has been pointed out that the radius of the dark space is decidedly greater than the calculated mean free path of the molecules. I have taken accurate measurements of the radius of the dark space at different pressures, and compared it with the calculated mean free path of the gaseous molecules at corresponding pressures when not under the influence of electrical energy, and I find that they do not bear a constant relation one to the other. The length of the dark space is not 20 times the mean free path, as some have estimated, but a gradually increasing multiple must be taken as the exhaustion becomes greater.

Exploration with Idle Poles.

Wishing to learn something of the electrical condition of the matter within and without the dark space, I made a tube (Fig. 7), having besides the positive and negative terminals, A, B, two extra intermediate poles, C and D; the tube showed that when the exhaustion was such that both the idle poles were outside the dark space, on passing the current through the tube, there was a considerable difference of potential between them when measured on the galvanometer. If the exhaustion was carried so high that one of the extra poles was just on the border of the dark space, then no current passed between them. When the exhaustion was still further increased so as to inclose one of the extra poles fully in the dark space, again there was a great difference of potential between them, but the direction was reversed, the pole at highest potential now being the one formerly at lowest potential.

When the dark space has been further explored by means of a movable negative pole, I found that the effects did not depend essentially on the exhaustion, and were really due to the position occupied by the extra pole with regard to the dark space.

These phenomena are difficult to understand from mere description, and the experiments themselves are not easy to carry out so as to be visible to many at a time. I have here, however, a working model of an apparatus which will make these puzzling indications clear to all.

A cylindrical tube (Fig. 8, a, b, and c, P. = 0.25 m.m.), furnished with the usual poles, A, B, at the ends, has two extra or idle poles near together at C and D. The pole A is movable along the axis of the tube, so that when exhausted the dark space can be brought to any desired position with respect to the idle poles C and D. The shading and + and - marks roughly show the distribution of positive and negative electricity inside the tube. I start with the negative pole A as far as possible from either idle pole (Fig. 8, a). Turning on the coil you see the dark space surrounding the pole A, and the idle poles quite outside.

The shading shows that each idle pole is in the positive area, and on testing with a gold leaf electroscope it will be seen that each is charged with positive electricity. But the shading also shows more positive at C than at D, and on connecting C and D with a galvanometer the needle indicates a rush of current from C to D, D being negative to C.

The dark space is next brought to such a position that the pole C is well within it (Fig. 8, b). A change has now come over the indications. The galvanometer shows a reverse current to that which was seen on the former occasion. C is now negative and D positive, but the gold leaves still tell us both poles are positively electrified.

At a certain position of the dark space, when its edge is on the pole C (Fig. 8, c), a neutral state is found at which the gold leaves still show strongly positive electrifications, and no current is seen on the galvanometer. The curves

below (Fig. 8, c), roughly show the rise and fall of negative and positive current at different parts of the tube, whilst the potential curve keeps positive.

When a substance that will phosphoresce under electrical excitement is introduced into the tube, the position of greatest luminosity is found to be at the border of the dark space, just where the two opposing armies of negative and positive atoms meet in battle array and recombine. Later on I shall refer to this phenomenon in connection with the phosphorescence of yttria.

(To be continued).

KEEPING OF "NESSLER" STANDARDS.

By W. P. MASON.

STANDARD tubes containing 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, and 0.09 m.grm. NH_3 in 50 c.c. water were prepared for use. Three days afterward they were compared with fresh standards of above values. It was observed that 0.03, 0.05, and 0.07 had not changed, and the remainder had darkened to a very slight degree—less than 0.0025 in each case.

Standards made in the morning may be thoroughly relied upon for working during the day.

NOTICES OF BOOKS.

An Introduction to the Study of Metallurgy. By Professor ROBERTS-AUSTEN, C.B., F.R.S. London: Charles Griffin and Co., 1891.

PROFESSOR ROBERTS-AUSTEN'S students have long hoped that he would give them in the form of a book his introductory Lectures on Metallurgy, in which he has for many years treated the subject in an original way. It was to be expected that he would take great pains in the preparation of such a volume, but we were hardly prepared to find so large a mass of information compressed into the small compass of a crown octavo volume.

His guiding principle seems to be that it is more important at the outset for the student to know what was the scope of mind of the early practisers of metallurgy, and to see what kind of aid the art may be expected to receive in future from the sciences, rather than to acquire familiarity with complicated details of processes and appliances. With this end in view he traces at some length the development of chemistry as a science from the very ancient metallurgical process of cupelling lead to extract the precious metals, and the opinions are given of prominent metallurgists and chemists from Geber in the eighth century to Lavoisier in the eighteenth, with abundant references to authorities.

Much space is devoted to a description of the action of minute quantities of elements on masses of metals, for Professor Roberts-Austen rightly considers the study of such questions to be the distinguishing feature of modern metallurgy. Indeed his own generalisation that the influence of "traces" on masses of metal is directly proportional to the atomic volume of the added element has been recognised as being the most important application from an industrial point of view which we have as yet had of the Periodic Law.

The number of curves he gives in illustration of this portion of his subject will be of great value to the student. Many of these have been specially prepared for this volume. Of similar value are the schemes showing the course adopted in conducting smelting operations. The scheme (p. 250) of the processes adopted in the great metallurgical district of Freiberg in Saxony for smelting complex ores, and the scheme (p. 242) for smelting ores of copper, deserve special mention.

A comprehensive classification of processes, and of the methods adopted in extracting metals from their ores, is given to show that the art of metallurgy is capable of being far more systematically treated than has hitherto been the case in this country. In dealing with typical metallurgical processes the author has hardly permitted himself sufficient space, and this portion of the volume, which is at present the least satisfactory, will, it may be hoped, be greatly extended in later editions.

The author considers that in the immediate future the most marked technical advance may be expected to arise, not from improvements in smelting operations, but from the study of the properties of metals and alloys as influenced by thermal and mechanical treatment, and by the presence of foreign matter. In this connection we welcome the introduction into the volume of Professor Austen's lecture delivered at Newcastle, on the "Hardening and Tempering of Steel," the merit of which has been so widely recognised. Its long array of references to authority will be found very serviceable; indeed, throughout the whole book the list of references is most complete.

From the point of view of the student the main question is, perhaps, how does this book differ from other books on the same subject? This we have to some extent already indicated, but it may be further pointed out that no text-book with which we are acquainted—at least no English text-book—at all approaches this one either in its method of treatment, its general arrangement, or in the completeness with which the most modern views on the subject are dealt with. The art of metallurgy is so rapidly changing from a more or less empirical application of chemistry and physics to an art of which both chemists and physicists are now looking for the explanation of many important but at present doubtful theoretical questions, that it is evident that a book of the nature of Professor Austen's volume will be invaluable, not only, as the author modestly describes it, to the student of metallurgy—using the term in its ordinary sense—but also to those whose knowledge of the art is far advanced.

Contributions of Alchemy to Numismatics. By HENRY CARRINGTON BOLTON, Ph.D. Read before the New York Numismatic and Archæological Society. Author's Edition: New York.

We have here a curious and interesting work, evidently the outcome of prolonged and careful research, the purport of which might have perhaps been more clearly understood had it been entitled "Contributions of Numismatics to the History of Alchemy." The author, though plainly no believer in the pretensions of the adepts, gives us some striking pictures of the alleged gold-makers of the seventeenth century.

There exist, it appears, a number of coins, medals, &c., said to have been stamped from bullion obtained by the Hermetic art. Many more such are recorded as having formerly existed. Of these pieces, forty-three are here particularly described. One of the most successful alchemists is said to have been Raymond Lully (Ramon Lulli, 1235 to 1315). This worthy is said to have transmuted base metals into gold, in the Tower of London and in Westminster Abbey, in such quantity that six million nobles, each exceeding £3 in value, were coined from the product. These coins, called "Raymond" or "Rose-nobles," are mentioned by Camden and Selden, and are said to have been of purer gold than that generally coined in the thirteenth century. Even if any of these pieces were still existent, there would be no evidence that they had been actually obtained from alchemical gold. The author quotes J. F. Buddeus to the effect that hermetic symbols upon a coin are no conclusive proof as to its origin. Reyher cites Monconys, to the effect that "The apothecary Strobelperger told me that a certain merchant of Lubeck, not very successful in business, but who knew how to 'fix' lead and convert it

into gold, presented to the King of Sweden a mass of gold weighing 100 lbs., prepared by himself through hermetic art. Gustavus Adolphus caused ducats to be made of this gold, bearing his likeness on one side and the Royal Arms, with the symbols of mercury and sulphur, on the other. He gave me (continues Monconys) one of these ducats, and said that after the death of the merchant, who did not seem very wealthy and had long since discontinued trade, 1,700,000 crowns were found in his house." This is a fine case of hearsay evidence!

Some of the leading alchemists of the seventeenth century were for a time successful, if not in making gold at least in obtaining it from their patrons. Wenzel Seyler was ennobled as Baron von Reinburg. Dr. Bolton has examined a medallion made from his gold in 1677. It is brassy in colour, and its specific gravity is only 12.67. Baron Krohnemann, a profligate and impudent swindler, was at length detected in fraud and was hanged by order of the Margrave of Brandenburg. Domenico Manuel, after a career of roguery, had the honour of being hanged on gilded gallows at Küstrin, in 1709.

Even the present century is not without its claimants of alchemical skill. Francois Cambriel, in 1843, undertook to teach the secret of transmutation in a course of 19 lessons. About the same time there was inserted in a leading London literary organ an advertisement offering to teach the "Hermetic art" for a fee of 100 guineas. In 1889 appeared in Paris the second edition of a work entitled "L'Or et la Transmutation des Metaux," by G. Théodore Tiffereau. He permitted one of the assayers of the Paris Mint to make an experiment according to his system. The result was negative. It is not likely that we shall have any more alchemists. Fraud and gullibility have entered upon novel phases.

CORRESPONDENCE.

REFERENCES TO ORIGINAL PAPERS.

To the Editor of the Chemical News.

SIR,—In your issue of October 3rd, 1890 (vol. lxii., p. 177, col. 2), "An Abstractor" justly complains of the carelessness of some authors in omitting the dates of publication of volumes to which references are made, and points out that vol. and page are insufficient.

Your correspondent remarks that the desired date can only be obtained by those who have "immediate access to a library round whose walls all journals ever published were properly ranged."

I cordially endorse his views as to the desirability of affixing dates to references, and beg leave to direct his attention to a compilation I published several years ago, which will enable him to determine the date of issue of any volume of each of 500 scientific periodicals without leaving his writing-desk. I refer to the extensive Chronological Tables accompanying my "Catalogue of Scientific and Technical Periodicals (1665-1882)," published by the Smithsonian Institution, as No. 514 of the Smithsonian Miscellaneous Collections, Washington, 1885. This catalogue forms an 8vo. volume of 773 pages, and comprises full titles of more than 5000 scientific periodicals in about twenty languages. Pages 618-707 contain the Chronological Tables, by the aid of which the year of publication of each volume of about 500 periodicals can be readily found, or, if the date be known, the number of the volume can be found. The sequence of several series, when a periodical has changed its name, or absorbed other journals, is also clearly indicated. These Chronological Tables have a separate index. I venture to describe this work here because I suspect all working savants are not familiar with this convenient hand-book. The Tables commence with the year 1728, and come down to the year 1880. The data for the decade just

closed are more easily obtained, and there are fewer irregularities of publication than in the earlier years. If your correspondent will send me his name and address, I shall be pleased to present him with a copy of my catalogue.—I am, &c.,

H. CARRINGTON BOLTON.

University Club, New York City.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., Part 1.

The Great Chemical Industries at the Exhibition of 1889.—M. P. Kienlen.—An account of the manufacture of sulphuric acid, and of the extraction of copper from the burnt ores.

On the Condensation of Gaseous Carbons under the Influence of the Effluve (Continued).—P. Schützenberger.—The gases which here come in question are carbon monoxide, cyanogen, mixtures of cyanogen and hydrogen, acetylene, and the vapour of benzene.

The Spontaneous Purification of Rivers with reference to the Waters of the Rhône.—P. Cazeneuve.—The spontaneous purification of rivers is a fact of constant occurrence. The Wupper is abominably contaminated at Elberfeld. Some miles lower down at Opladen it is pure, and serves for the most delicate uses of the dye works, which require very pure waters. The Isar receives at Munich the filth of forty-nine sewers. Below Munich the river rapidly becomes pure, as is proved by the analysis of Schelbass, Brunner, and Emmerick. The Derle receives the waste waters of Lille, coming from paper-mills, distilleries, and starch works. The water takes an impure character visible to the naked eye, but which gradually disappears. The same phenomenon of purification is seen in the Rhône. The dyers of the Quay Saint Clair turn into the river their waste liquors, and when they empty their becks the waters are coloured all the length of the quay for a breadth of 25 or 30 metres. A kilometre lower down at the Morand Bridge, the Rhône is perfectly limpid. When hypochlorites or *Cocculus indicus* is thrown into a river at 2 or 3 kilometres lower down the fishes are not injured. The two drains of Clichy and St. Denis pour into the Seine 3 cubic metres per second of polluted water, whilst at Meudon every trace of infection has disappeared.

Influence of Silicon on the Properties of Iron and Steel.—Th. Turner.—From the *Journal of the Chemical Society*.

The Use of Fluor-spar in Metallurgy.—Dr. Foehr. An abridgment from the *Chemiker Zeitung*.

Quantities of Zinc and Lead Contained in the Gases of Blast Furnaces.—Albert Nita (*Zeitschrift Angewandte Chemie*).—The quantity of zinc thus carried off corresponds to 27 per cent of the total amount in the ore. The loss of lead is only 9 per cent.

Metallurgy in the West of America.—R. Pearce.—An account of the operations of the Boston and Colorado Smelting Company.—*Chemiker Zeitung*.

Mercury Mine at Nikitowka, in Russia.—C. Ernst (from the *Chemiker Zeitung*).—The yield of mercury was in 1887 63,967 kilos., and in 1888 it had risen to 164,790 kilos.

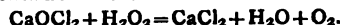
The O'Brien Process for the Extraction of Gold and Silver from Pyrites.—(*Chemiker Zeitung*).—The ore is roasted, treated for twenty-four to thirty hours with sulphurous anhydride, washed with water, and amalga-

mated in the ordinary manner. The quantity of silver extracted is much more considerable than by the chloruration process. The sulphurous acid is obtained by roasting the ore.

Analysis of Manganese by Means of Hydrogen Peroxide.—A. Baumann (*Zeit. Angewandte Chem.*).—If manganese peroxide in powder is allowed to act upon hydrogen peroxide in a neutral or alkaline solution, the hydrogen peroxide is decomposed, oxygen is set at liberty, but the manganese is not attacked. If the hydrogen peroxide is in an acid solution and in excess, the manganese dioxide is reduced to the state of a salt of the monoxide, and oxygen is given off proportionate to the weight of MnO_2 present; 86.72 MnO_2 yield 31.92 of oxygen. Three methods may be founded upon this reaction: gravimetric, volumetric, and the direct determination of the gas given off.

Detection of Sodium Thiosulphate in Sodium Bicarbonate.—J. Lüttke (*Chemiker Zeitung*).—If we add a few c.c. of a solution of barium nitrate to a solution of sodium bicarbonate previously saturated with hydrochloric acid and not containing sulphuric acid, no turbidity or precipitate ought to be occasioned. If a thiosulphate is present, there is formed a turbidity or a precipitate on adding a drop of permanganate, which transforms the thiosulphate into a sulphate.

Use of the Nitrometer for Titrating Chloride of Lime, Manganese, and Permanganate.—G. Lunge (*Zeit. f. Angewandte Chem.*).—The method, which was described some years ago, is founded on the use of oxygenated water. In the case of chloride of lime a volume of oxygen is evolved equal to the volume of the active chlorine contained in the chloride—



NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Magnesium Chloride.—Can any reader inform me how chloride of magnesium, used for sizing purposes in Lancashire, is manufactured?—W. H. B.

MEETINGS FOR THE WEEK.

- MONDAY, 9th.—Medical, 8.30.
Society of Arts, 8. "The Construction and Capabilities of Musical Instruments," by A. J. Hipkins, F.S.A.
- TUESDAY, 10th.—Institute of Civil Engineers, 8.
Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley, F.R.S., B.S., F.R.C.S., Fullerian Professor of Physiology, R.I.
Photographic, 8 (Anniversary).
Royal Medical and Chirurgical, 8.30.
Society of Arts, 8. "Sgraffito," by Heywood Sumner.
- WEDNESDAY, 11th.—Society of Arts, 8. "The Proposed Irish Channel Tunnel," by Sir Robert Lethbridge, M.P.
Pharmaceutical, 8.
- THURSDAY, 12th.—Royal, 4.30.
Mathematical, 8.
Institute of Electrical Engineers, 8.
Royal Institution, 3. "The Position of Lull, Purcell, and Scarlatti in the History of the Opera," by Professor C. Hubert H. Parry, Mus. Doc. M.A.
- FRIDAY, 13th.—Royal Institution, 9. "Some Results of Recent Eclipse Expeditions," by Professor A. Schuster, Ph.D., F.R.S., F.R.A.S.
Astronomical, 3. (Anniversary).
Physical, 5. Annual General Meeting. (1) "Discussion of Prof. Minchin's Paper on Photo-electricity;" (2) "The Change in the Absorption Spectrum of Cobalt Glass Produced by Heat," by Sir John Conroy, Bart., M.A.
- SATURDAY, 14th.—Royal Institution, 3. "The Forces of Cohesion," by The Right Hon. Lord Rayleigh, M.A., D.C.L., F.R.S.

THE CHEMICAL NEWS.

VOL. LXIII., No. 1629.

NOTE ON ALDEPALMITIC ACID, THE CHIEF CONSTITUENT OF THE BUTTER OF THE COW

By J. ALFRED WANKLYN.

ON the 19th of last month I had the honour of laying before the Society of Chemical Industry a short account of my investigations into the nature and constitution of butter, and made the announcement that the commonly received views of the constitution of butter are erroneous. It does not consist mainly of olein, palmitin, and stearin, but of something quite different from the common animal and vegetable fats.

The chief acid in butter soap is not palmitic acid, but a new acid to which I have given the name aldepalmitic acid. This acid differs from palmitic acid by containing less hydrogen (as was shown by a combustion of the substance), and by its equivalent being smaller (shown by most careful investigation of its baryta-salt).

Its formula appears to be $(C_{16}H_{30}O_2)_n$; but it does not belong to the oleic series of acids. I expect that its molecule will turn out to be very complex, and that the n in the formula will be at least 2.

Between the properties of the new acid and those of palmitic acid obtained from palm oil the differences are very striking.

The specific gravities are different and the melting-points different, and nothing could well be more striking than the behaviour of the two acids towards alcohol of 85 per cent strength.

At ordinary temperatures the solubility of the acids is very nearly the same, but as the temperature rises the differences appear. The solubility of palmitic acid increases, comparatively slowly, as the temperature rises; but the solubility of aldepalmitic acid jumps up suddenly, so that at 25° C. this acid passes into perfect solution in about its own weight of alcohol. When the alcoholic solution is cooled down to common temperatures, the entire solution solidifies or gelatinises, and in that manner aldepalmitic acid can solidify five times its weight of alcohol. Part of the alcohol is retained mechanically and part chemically.

On the other hand, palmitic acid possesses no power of combining with alcohol. Some of the salts of aldepalmitic acid combine readily with a large proportion of alcohol. In fine, aldepalmitic acid is a most distinct substance endowed with most characteristic properties.

LOSS OF CARBON IN RUSTED PIG-IRON.

By J. G. DONALD, M.A.

RECENTLY the writer was engaged in determining the graphite and carbon in two samples of pig-iron. The drillings weighed off for treatment with cuprammonium chloride were brushed into beakers which were wet, having been rinsed with distilled water. At this point, and before the solvent had been added, he was called away. On returning to the work, after the lapse of nearly a week, the drillings in the beakers were of course found to be much rusted.

The idea occurred to him that it would be interesting to learn to what extent there had been loss of carbon

through the rusting of the drillings. To this end the rusted portions as well as portions of the original samples were treated with the solvent, and the carbon sponge submitted to combustion, with the following results for total carbon:—

	No. 1.	No. 2.
Rusted drillings ..	1'941	1'332
Original sample..	2'282	2'132

The combined carbon in each of the samples was found to be as follows:—

No. 1.	No. 2.
0'378	0'336

It will thus be seen that in the case of No. 2 the rusting has caused a disappearance of a portion of the graphite. No. 2 was in much finer drillings than No. 1, and to this fact is doubtless due in part at least the greater loss of carbon in No. 2.

124, St. James Street,
Montreal, Canada, January 21, 1890.

THE POTASSIUM CYANIDE ASSAY OF LEAD ORES.

By WALTER J. COOPER.

REFERRING to the article on "The Potassium Cyanide Assay of Lead Ores" (CHEMICAL NEWS, vol. lxii., p. 30). I notice that in the experiments (15 and 16), made with the ores containing pyrites, the author does not say what becomes of the copper present, and the general wording of the article seems to state that the reduced lead was obtained as a clean weighable button, which result I cannot reconcile with my own experience.

During last autumn I made some experiments with galena and pyrites bearing quartz from North Wales, of which the following is the average analysis—

SiO ₂	83'05
Fe ₂ S ₃ Cu ₂ S	10'639
FeS ₂	2'967
PbS	3'001
Au.. ..	Trace (Not estimated.)
Fe ₂ O ₃	0'343
	100'000

Among other experiments I tried the reduction of the ore by means of potassium cyanide. The ordinary commercial cyanide was used, being mixed with the ore in very large excess. A Battersea crucible was taken, and a thick layer of cyanide well rammed into the bottom; the mixed ore and cyanide were then introduced, and the whole well covered with cyanide. The charge was heated at a moderate red heat till the evolution of gas had nearly ceased, and the whole then raised to a bright red heat for a further five minutes and allowed to cool.

The crucible was then broken, and the slag which was black and very hard removed by boiling with water. The fine black mud (Fe) was then washed carefully away and a small button of lead with numerous scales of copper remained in the bottom of the beaker. The button was rather hard and the surface covered with strongly adhering copper scales. On analysis it proved to contain all the lead with a considerable quantity of copper and a little iron.

The above results seem to point out that with lead ores containing other reducible metals, the assay by means of potassium cyanide offers no advantages over the ordinary means of estimation by the wet method, as the resulting button has to be carefully analysed in order to ascertain the actual quantity of lead present.

High Street, Mitcheldean.

The crystals are large and well-formed and differ in size; they lie about two feet below the level of the marsh under a crust composed of sulphate of soda, carbonate of soda, and salt, and are pure enough for roasting, containing 95 per cent of borax, and yielding when calcined 180 per cent borax.

The geological formation of the surrounding hills consists of granite, marble, dolomite, black lava, and felspar; the sand of the valley is mixed with volcanic ash and decomposed lime rock. Many theories have been laid down as to the formation of the borax. Sesquiborate of lime ($\text{Ca}_2\text{B}_6\text{O}_{11}$), is slightly soluble in water, and when treated with carbonate or bicarbonate of soda, may be converted into borax.

Sesquiborate of lime ($\text{Ca}_2\text{B}_6\text{O}_{11}$), with five molecules of water, is the composition of different varieties of borate of lime that are at present used in the manufacture of borax. When this is heated in a current of steam, boracic acid passes off; in fact, when heated by itself the steam arising from the water of combination is sufficient to carry with it free boracic acid.

In California, as in Asia Minor, beds of this sesquiborate of lime are found which crop out on the surface, or are found at different depths below the surface. This sesquiborate of lime may consequently be the source from which the boracic acid comes.

In Saline Valley there are depressions or circular holes which have the appearance of extinct fumaroles, where subterranean gases and vapours may have passed into the waters of the lake. It is possible that vapours carrying boracic acid, as we find is the case in the Tuscan boracic acid lagoons, may have percolated into the waters of the lake, which, being strongly alkaline, have converted the boracic acid into borax, and the lake subsequently drying up the borax was left. Or the borax may have been formed by the direct action of alkaline waters of the lake on the borate of lime found within the area covered by the lake.

The formation or manufacture of borax by artificial means is an industry carried on in different parts of the world. The material most extensively used is the sesquiborate of lime, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{aq}$, known as pandermite, colemanite, boracite, or priceite. When this material is decomposed with carbonate of soda, which may be done by bringing them together in contact with water, double decomposition takes place—



The borate of soda, NaBO_2 , crystallises from syrupy solutions in needle-shaped crystals, having the formula $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$, and the composition being—

Boracic acid, B_2O_3	..	..	25.3
Soda, Na_2O	..	..	22.5
Water, H_2O	..	..	52.2
			100.0

Borate of soda may be formed by mixing the concentrated solutions of borax and caustic soda in their equivalent quantities and evaporating to a syrupy consistency, $\text{Na}_2\text{B}_4\text{O}_7 + 2\text{NaHO} = 4\text{NaBO}_2 + \text{H}_2\text{O}$. Borate of soda is decomposed by carbonic acid, forming borax and carbonate of soda, $4\text{NaBO}_2 + \text{CO}_2 = \text{Na}_2\text{B}_4\text{O}_7 + \text{Na}_2\text{CO}_3$.

In the conversion of sesquiborate of lime into borax by means of carbonate of soda, large quantities of this borate of soda are formed.

As borax is frequently tested volumetrically, and the boracic acid calculated accordingly, it is well to prove the absence of the borate of soda in the first place, as the higher percentage of soda the borate of soda contains might lead to erroneous results.

The following comparative table of the crystalline and anhydrous salts will show the relative difference between the two:—

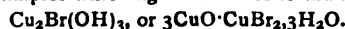
	Biborate of soda.	Borate of soda.	Biborate of soda, crystal'd.	Borate of soda, crystal'd.
Boracic acid, B_2O_3	69.05	53.03	36.6	25.3
Soda, Na_2O	30.95	46.97	16.2	22.5
Water, H_2O	—	—	47.2	52.2
	100.00	100.00	100.0	100.0

ON CUPRIC OXYBROMIDE.*

By THEODORE WILLIAM RICHARDS.

A CAREFUL examination of the basic bromide of copper precipitated by the solution of dried cupric bromide in water being an essential consideration in the preceding research upon the atomic weight of copper, a quantity of the substance was gradually collected from successive preparations for the purpose of analysis.

The only mention of the preparation of a definite oxybromide of copper in chemical literature is that by Et. Brun,† who obtained a crystalline salt by the slow oxidation of a solution of cuprous bromide in aqueous potassic bromide, as well as by the action of the latter salt upon ammoniacal cupric sulphate. He describes his new preparation as consisting of very small dark green crystals totally insoluble in water, and gives several analyses of different samples which agree with the formula—



It seemed very probable that the substance under discussion was identical with this body, although prepared in a very different manner.

The oxybromide so often mentioned in the foregoing description of the research upon the atomic weight of copper crystallises in very beautiful doubly-terminated prisms which undoubtedly belong to the trimetric system, and have the varying habit shown in the accompanying sketch. When precipitated by the rapid addition of water to solid slightly basic copper bromide, the prisms appear as extremely thin plates (Fig. 1), often united in radiating groups; but on more gradual crystallisation from stronger brown solutions, the crystals develop nearly equally in all axial directions (Figs. 2 and 3). The only angle even approximately measured with success by means of the microscope was that of the two domes upon each other, giving an inclination of about $94\frac{1}{2}^\circ$ between the normals. This value affords us the means of calculating the axial ratio, $x : z = 1 : 1.08$; and the two figures suggest the angle $96^\circ 38'$ and axial ratio $1 : 1.123$ observed in atacamite.‡ Indeed, the general resemblance in habit and in emerald green colour between the two substances is very marked, and has already been noticed by Brun.§

Crystallised cupric oxybromide which has been dried in the air does not lose weight over sulphuric acid. It is, of course, very soluble in mineral acids and in ammonia, as well as in strong acetic acid. The mode of formation of the salt shows that it must be slightly soluble also in very concentrated solutions of the normal cupric bromide, and that dilution diminishes, or perhaps wholly destroys, this solubility. The proof of its total insolubility in water being of great importance in the preceding research, the following experiment was made.

Two hundred c.c. of water were digested for four days at 25° with a tenth of a grm. of very fine crystals of copper oxybromide, the mixture being occasionally shaken. The liquid was then filtered, and 30 c.c. contained in a

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, Vol. xxv.

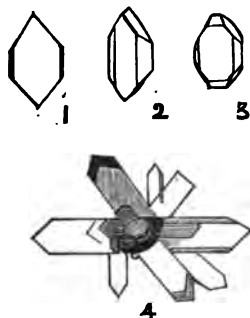
† *Compt. Rend.*, vol. cix., p. 66 (1889). Lwig and Berthelot describe an indefinite substance. *Liebig's Handw. Ch.*, iv. 714; *Ann. de Chim. et de Phys.*, [iii.] xlv. 365.

‡ Zepharovich, *Wien. Akad. Sitzungsber.*, 1871 ol. lxiil., Part I., p. 6.

§ *Loc. cit.*

long tube were tested for copper with ammonia, giving an absolutely negative result. 130 c.c. of the same liquid were evaporated to dryness, and the apparently clean dish was rinsed with a few drops of dilute nitric acid, to which was then added an excess of ammonia. An exceedingly faint tinge only of blue was apparent, much less than that produced by one-tenth of a m.grm. of copper under the same circumstances.

Being thus essentially insoluble in water, the oxybromide could hardly be present, even in traces, in the very dilute solution of cupric bromide used for the determination of the atomic weight; but for certainty upon this point the normal state of this solution was tested by experiments with methyl orange. These experiments, which have already been described,* settled the question in a wholly satisfactory manner.



Magnified 250 diameters.

The salt is decomposed by continued boiling with water into the normal bromide and a dark insoluble compound of uncertain composition. Brun has already pointed out the fact that the crystals are quite decomposed when heated to 250°.

On account of the very small amount of substance at hand, the analysis was undertaken with all possible care.

- I. 0.20003 grm. of copper oxybromide yielded, on evaporation with nitric and sulphuric acids and subsequent electrolysis, 0.09823 grm. of metallic copper.
- II. 0.0828 grm. of copper oxybromide yielded, on solution in ammonia, acidification with nitric acid, and precipitation by silver nitrate, 0.0606 grm. of argentic bromide.

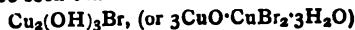
Analysis of Cupric Oxybromide.

	Theory, $\text{Cu}_2(\text{OH})_2\text{Br}$.	Found.	
		I.	II. Brun's results.
Copper	49.27	49.11	49.19
Bromine	30.98	—	31.15 31.05

The results agree with the theoretical as well as could be expected, considering the small quantities of substance used.

By the very slow oxidation of cuprous bromide, kept under water in the dark for six months, groups of emerald green radiating prisms over a tenth of a m.m. in length were obtained (Fig. 4), which, by their terminal angles, colour, and general appearance, showed themselves to be identical with the compound whose analysis has just been given. The amount of these crystals was so small that it was impossible to determine their percentage composition, but there can be no doubt of its agreement with that given above. The crystalline salt was also obtained by the long-continued action of cupric oxide upon a strong solution of cupric bromide.

It will be seen that the formula—



does not exactly correspond to that of any one of the known oxychlorides, containing only three-fourths as much water as atacamite ($3\text{CuO} \cdot \text{CuCl}_2 \cdot 4\text{H}_2\text{O}$). It is a noteworthy fact, however, that many of the more definite basic salts of copper contain, as these do, three molecules of copper oxide to every single molecule of the normal compound.

CIRCULAR ON ATOMIC WEIGHTS.

By request of the Committee of Revision and Publication of the Pharmacopœia of the United States of America, Prof. F. W. Clarke, Chief Chemist of the U.S. Geological Survey, has furnished a Table of Atomic Weights, revised upon the basis of the most recent data, and his latest computations. The Committee has resolved that this Table be printed and furnished for publication to the professional press. The Committee also requests that all calculations and analytical data which are to be given in reports or contributions intended for its use or cognisance, be based upon the values in the Table. It would be highly desirable that this Table be adopted and uniformly followed by chemists in general, at least for practical purposes, until it is superseded by a revised edition. It would only be necessary for any author of a paper, &c., to state that his analytical figures are based upon "Prof. Clarke's Table of Atomic Weights, of Dec. 6th, 1890," or some subsequent issue.

CHARLES RICE,
Chairman of the Committee of Revision, &c.

New York, Dec. 20, 1890.

TABLE OF ATOMIC WEIGHTS.

(Issued December 6, 1890.)

Revised for the Committee of Revision and Publication of the Pharmacopœia of the United States of America.

By F. W. CLARKE,
Chief Chemist of the United States Geological Survey.

THIS Table represents the latest and most trustworthy results, reduced to a uniform basis of comparison, with oxygen = 16 as starting-point of the system. No decimal places representing large uncertainties are used. When values vary, with equal probability on both sides, so far as our present knowledge goes, as in the case of cadmium (111.8 and 112.2), the mean value is given in the Table.

The names of elements occurring in pharmacopœial, medicinal, chemicals, are printed in *italics*.

Name.	Symbol.	Atomic weight.
<i>Aluminum</i>	<i>Al</i>	27.
<i>Antimony</i>	<i>Sb</i>	120.
<i>Arsenic</i>	<i>As</i>	75.
<i>Barium</i>	<i>Ba</i>	187.
<i>Bismuth</i>	<i>Bi</i>	208.9
<i>Boron</i>	<i>B</i>	11.
<i>Bromine</i>	<i>Br</i>	79.95
<i>Cadmium</i>	<i>Cd</i>	112.
<i>Cæsium</i>	<i>Cs</i>	132.9
<i>Calcium</i>	<i>Ca</i>	40.
<i>Carbon</i>	<i>C</i>	12.
<i>Cerium</i>	<i>Ce</i>	140.2
<i>Chlorine</i>	<i>Cl</i>	35.45
<i>Chromium</i>	<i>Cr</i>	52.1
<i>Cobalt</i>	<i>Co</i>	59.
* <i>Columbium</i>	<i>Cb</i>	94.
<i>Copper</i>	<i>Cu</i>	63.4
† <i>Didymium</i>	<i>Di</i>	142.3
<i>Erbium</i>	<i>Er</i>	166.3
<i>Fluorine</i>	<i>F</i>	19.
<i>Gallium</i>	<i>Ga</i>	69.
<i>Germanium</i>	<i>Ge</i>	72.3

Name.	Symbol.	Atomic weight.
Glucinum	Gl	9 [*]
Gold	Au	197.3
Hydrogen	H	1.007
Indium	In	113.7
Iodine	I	126.85
Iridium	Ir	193.1
Iron	Fe	56 [*]
Lanthanum	La	138.2
Lead	Pb	206.95
Lithium	Li	7.02
Magnesium	Mg	24.3
Manganese	Mn	55 [*]
Mercury	Hg	200 [*]
Molybdenum	Mo	96 [*]
Nickel	Ni	58.7
Nitrogen	N	14.03
Osmium	Os	191.7
Oxygen	O	16 [*]
Palladium	Pd	106.6
Phosphorus	P	31 [*]
Platinum	Pt	195 [*]
Potassium	K	39.11
Rhodium	Rh	103.5
Rubidium	Rb	85.5
Ruthenium	Ru	101.6
Samarium	Sm	150 [*]
Scandium	Sc	44 [*]
Selenium	Se	79 [*]
Silicon	Si	28.4
Silver	Ag	107.92
Sodium	Na	23.05
Strontium	Sr	87.6
Sulphur	S	32.06
Tantalum	Ta	182.6
Tellurium	Te	125 [*]
Terbium	Tb	159.5
Thallium	Tl	204.18
Thorium	Th	232.6
Tin	Sn	119 [*]
Titanium	Ti	48 [*]
Tungsten	W	184 [*]
Uranium	U	239.6
Vanadium	V	51.4
Ytterbium	Yb	173 [*]
Yttrium	Yt	89.1
Zinc	Zn	65.3
Zirconium	Zr	90.6

* Has priority over niobium.

† Now split into neo- and praseo-didymium.

‡ Has priority over beryllium.

§ Standard, or basis of the system.

Researches on Alizarin Oil.—M. Scheurer-Kestner.—The author arrives at the following conclusions:—The oil for red tones is formed of sulphuricinoleic acid, a compound which is definite and permanent at the ordinary temperature. It is accompanied by polyricinic acids, the condensation of which extends as far as to di-ricinic acids. The molecular weights, which the author has found by Raoult's method, employing the substance dissolved in acetic acid, indicate a mixture of mono- and di-ricinic acids. The sulpho-fatty compound is hydrated, and is stable in the hydrous state. It loses its water of hydration completely at about 120 and becomes insoluble. It is resolved into hydrated sulphuric acid and an oily acid. From the tinctorial point of view, the author has recognised an interesting fact:—That the sulphonic compound gives shades inclining to a yellow, whilst the polymerised fatty acids give a carmine shade verging more towards a blue.—*Comptes Rendus*, Vol. cxii., No. 3.

On Sizing Paper according to the Most Recent Practical Experience.—Dr. E. Muth (*Dingler's Journ.*).—A very full account of the preparation and application of the sizes used by paper-makers, those especially in which resin soaps play a leading part.—*Monit. Sci.*

ELECTRICITY

IN TRANSITU: FROM PLENUM TO VACUUM.*

By WILLIAM CROOKES, F.R.S.,
President of the Institution of Electrical Engineers.

(Continued from p. 70).

Radiant Matter.

By means of this tube (Fig. 9), I am able to show that a stream of ultra-gaseous particles, or Radiant Matter, does not carry a current of electricity, but consists of a succession of negatively electrified molecules whose electrostatic repulsion overbalances their electro-magnetic attraction, probably because their speed along the tube is less than the velocity of light. The tube has two negative terminals, A, A', close together at one end, enabling me to send along the tube two parallel streams of radiant matter, rendered visible by impinging them through holes in a mica diaphragm on a screen of phosphorescent substance. It is exhausted to a pressure of 0.1 m.m. I connect one of the negative poles, A, with the induction coil and the luminous stream darts along the tube from c to d parallel with the axis. I now connect the other negative pole, giving a second parallel stream of radiant matter. If these streams are in the nature of wires carrying a current they will attract each other, but if they are simply two streams of electrified molecules they will repel each other. As soon as the second stream is started you see the first stream jump away in the direction c, z, showing strong repulsion, proving that they do not act like current carriers, but merely like similarly electrified bodies. It is, however, probable that were the velocity of the streams of molecules greater than that of light, they would behave differently, and attract each other, like conductors carrying a current.

To ascertain the electrical state of the residual molecules in a highly exhausted tube such as you have just seen, I introduced an idle pole or exploring electrode between the positive and negative electrodes in such a manner that the molecular stream might play upon it. The intention was to ascertain whether the molecules on collision with an obstacle gave off any of their electrical charge. In this experiment (Fig. 10, P.=0.0001 m.m., or 0.13 M.†) it was found that an idle pole, c, placed in the direct line between the positive and the negative poles, A, B, receiving in consequence the full impact of the molecules shot from the negative pole, manifested a strong positive charge. In a variety of other experiments made to decide this question, the electricity obtained was always found positive on testing with the gold leaf or Lippman's electrometer, and when the idle pole was connected to earth through a galvanometer a current passed as if this pole were the copper element of a copper-zinc cell, indicating leakage of a current to earth, the idle pole being positive. If, instead of sending this current to earth, the wire was connected to the negative pole of the tube, a much more powerful current passed in the same direction.

The Edison Effect.

An exactly parallel experiment has been made by Mr. Edison, Mr. Preece, F.R.S., and Prof. Fleming, using, instead of a vacuum tube, an incandescent lamp. They found that from an idle pole placed between the ends of the filament the electricity always flowed as if the pole were the zinc element of a copper-zinc cell; having repeated their experiments I entirely corroborate them. I get a powerful current in one direction from an idle pole placed between the limbs of an incandescent carbon filament, and one in the opposite direction from an idle pole in an highly exhausted vacuum tube. This discrepancy

* Inaugural Address delivered January 13th, 1891.

† M. = one-millionth of an atmosphere.

1,000,000 M. = 760 m.m.

= one atmosphere.

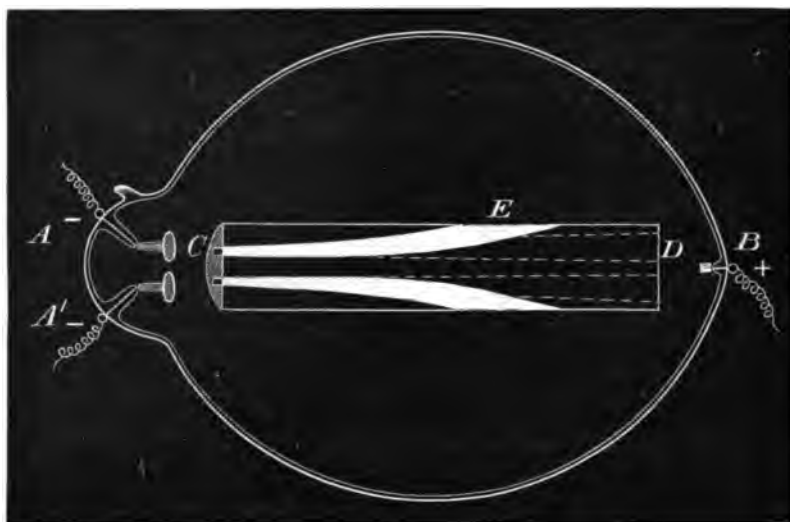


FIG. 9.—P. = 0.1 m.m.

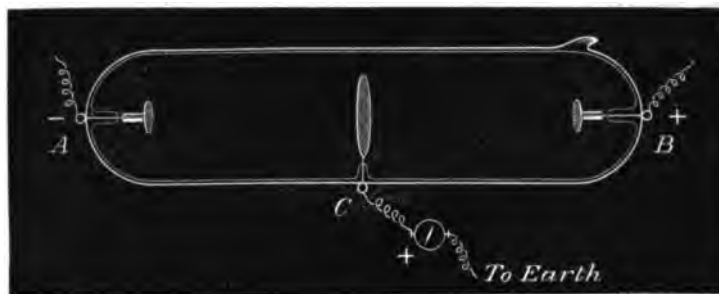


FIG. 10.—P. = 0.0001 m.m., or 0.13 M.

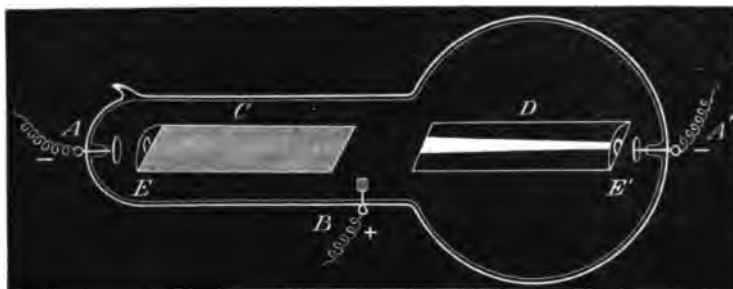


FIG. 11.—P. = 0.001 m.m., or 1.3 M.

was extremely puzzling, and I tested, with a similar result, very many experimental tubes made in different ways. The electricity obtained from an idle pole placed between the positive and negative terminals in a highly exhausted tube was always strongly *positive*, and it is only recently that continued experiment has cleared the matter up.

Some of the contradictory results are due to the exhaustion not being identical in all cases. In my vacuum tubes the directions of current between the idle pole and the earth changes from negative to positive as the exhaustion rises higher. Testing the current when exhaustion is proceeding, there is a point reached when the galvano-

meter deflection—hitherto negative—becomes nil, showing that the potential at this point is zero. At this stage the passage of a few more drops of mercury down the pump tube renders the current positive. This change occurs at a pressure of about 2 m.m.

After this point is reached, when the induction current is passed through the tube, the walls rapidly become positively electrified, probably by the friction of the molecular stream against the glass, and this electrification extends over the surface of any object placed inside the tube. I will show you how this electrification of the inner walls of the tube acts on the molecular stream at high

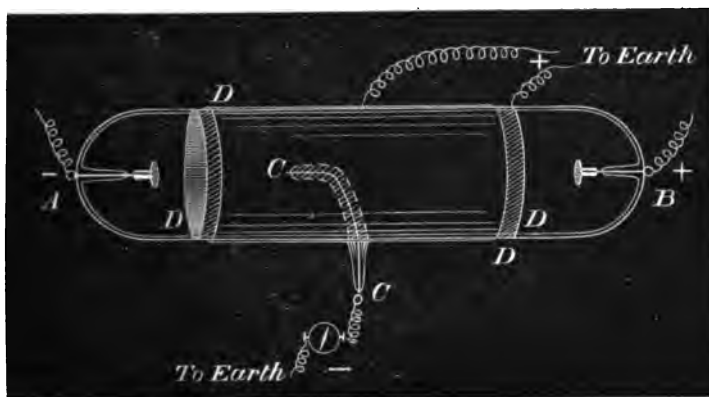


FIG. 12.—P. = 0.0001 m.m., or 0.13 M.

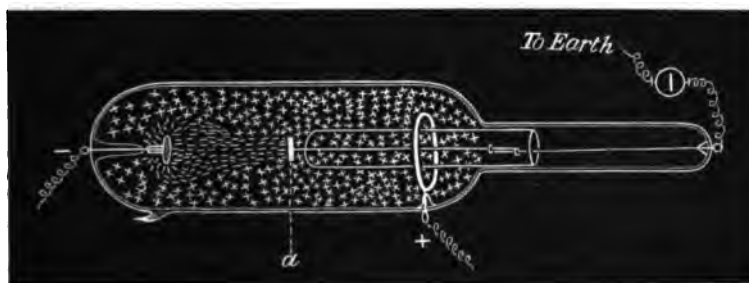


FIG. 13a.—P. = 0.0001 m.m., or 0.13 M.

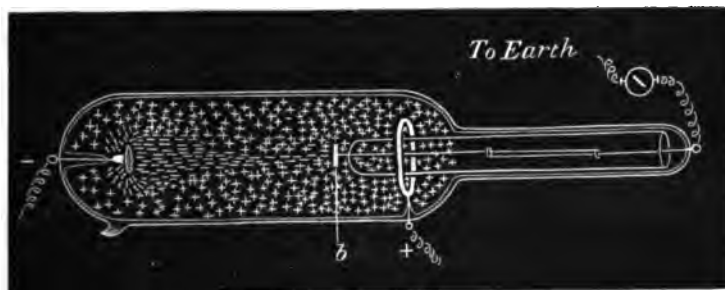


FIG. 13b.—P. = 0.0001 m.m., or 0.13 M.

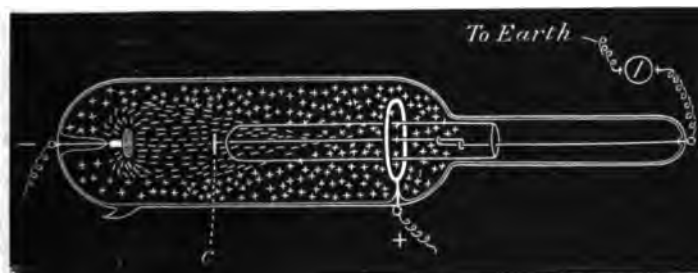


FIG. 13c.—P. = 0.0001 m.m., or 0.13 M.

vacua. In this tube, Fig. 11 ($P = 0.001$ m.m., or 1.3 M.), are fixed to exactly similar phosphorescent screens, c and d ; at one end of each is a mica gate, x, x' , with a negative pole, A, A' , facing it. One of the screens, c , is in the cylindrical part of the tube and close to the walls; the other, d , is in the spherical portion, and therefore far removed from the walls. On passing the current the screen d in the globe shows a narrow sharp streak of phosphorescence, proving that here the molecules are free to follow their normal course straight from the negative pole. In the cylindrical part of the tube, however, so great is the attraction of the walls that the molecular stream is widened out sufficiently to make the whole surface of the screen, c , glow with phosphorescent light.

If an idle pole, c, c' , Fig. 12 ($P = 0.001$ m.m., or 0.13 M.), protected all but the point by a thick coating of glass, is brought into the centre of the molecular stream in front of the negative pole A , and the whole of the inside and outside of the tube walls are coated with metal, D, D , and "earthed," so as to carry away the positive electricity as rapidly as possible, then it is seen that the molecules leaving the negative pole and striking upon the idle pole c on their journey along the tube carry a negative charge, and communicate negative electricity to the idle pole.

This tube is of interest since it is the one in which I was first able to perceive how in my earlier results I always obtained a positive charge from an idle pole placed in the direct stream from the negative pole. Having got so far, it was easy to devise a form of apparatus that completely verified the theory, and at the same time threw considerably more light upon the subject. Fig. 13, a, b, c , is such a tube, and in this model I have endeavoured to show the electrical state of it at a high vacuum by marking a number of + and - signs. The exhaustion has been carried to 0.0001 m.m., or 0.13 M., and you see that in the neighbourhood of the positive pole, and extending almost to the negative, the tube is strongly electrified with positive electricity, the negative atoms shooting out from the negative pole in a rapidly diminishing cone. If an idle pole is placed in the position shown at Fig. 13 a , the impacts of positive and negative molecules are about equal, and no decided current will pass from it, through the galvanometer, to earth. This is the neutral point. But if we imagine the idle pole to be as at Fig. 13 b , then the positively electrified molecules greatly preponderate over the negative molecules, and positive electricity is shown. If the idle pole is now shifted as shown at Fig. 13 c , the negative molecules preponderate, and the pole will give negative electricity.

As the exhaustion proceeds, the positive charge in the tube increases, and the neutral point approaches closer to the negative pole, and at a point just short of non-conduction so greatly does the positive electrification preponderate that it is almost impossible to get negative electricity from the idle pole, unless it actually touches the negative pole. This tube is before you, and I will now proceed to show the change in direction of current by moving the idle pole.

I have not succeeded in getting the "Edison" current in incandescent lamps to change in direction at even the highest degree of exhaustion which my pump will produce. The subject requires further investigation, and like other residual phenomena these discrepancies promise a rich harvest of future discoveries to the experimental philosopher, just as the waste products of the chemist have often proved the source of new and valuable bodies.

(To be continued).

New Process of Bleaching.—This process depends on the decolourising action of certain products of the distillation of bituminous shales upon all fibrous matters with which they are boiled. The quantity of oil used per ton varies from 4.5 to 9 litres, according to the quality of the material.—*Moniteur Scientifique*, iv., Part 1.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 15th, 1891.

Dr. W. J. RUSSELL, F.R.S., in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Henry Austin Appleton, 19, South Street, Middlesbrough; John Charles Aydans, 44, Crescent Road, Plumstead, S.E.; Clayton Beadle, Beadonwell, Belvedere, Kent; Thomas Byrne, Glenville, Dundrum, co. Dublin; Arthur Cole, B.A., Holmleigh, Charles Street, Berkhamstead; Reginald Lorn Marshall, 25, Lancaster Park, Richmond; Tom Kirke Rose, 9, Royal Mint, E.; R. Greig Smith, Springwells, New Street, Musselburgh; Howard C. Sucié, Breeze House, Higher Broughton, Manchester; Matthew Carrington Sykes, Sykeahurst, Barnsley, Yorks; W. Will, Ph.D., 1, Beethoven Strasse, Berlin, N.W.

The following papers were read:—

1. "Magnetic Rotation." By W. OSTWALD.

The magnetic rotation of organic compounds, according to Perkin, is an additive function of their composition and equal to the sum of the rotations of the components, but this is not the case with the rotation of inorganic compounds, which is usually found greater than that calculated on such an assumption. In the case of hydrogen chloride, for instance, the calculated value is about 2.18 , and as a matter of fact the value obtained for hydrogen chloride dissolved in an organic solvent, isoamyl oxide, is 2.24 , but when dissolved in water the value found is from 4.05 to 4.42 , increasing with the dilution. The author points out that these exceptional values are only obtained in the case of electrolytes, and that they must therefore be referred to a fundamental difference existing between the constitution of electrolytes and that of non-conductors. That such a difference exists has been already deduced from other considerations, and has led Arrhenius to the formulation of the theory of electrolytic dissociation. The author claims that the facts established with regard to magnetic rotation are in perfect accordance with this theory, and that any exceptional values in the magnetic rotations of electrolytes are due to the occurrence of electrolytic dissociation.

DISCUSSION.

Mr. PICKERING said that in Professor Ostwald's attempt to appropriate Dr. Perkin's results on the magnetic rotation of solutions of electrolytes in support of the dissociation theory, no attempt was made to explain what connection should exist between the magnetic rotation and the supposed dissociation into ions, but it was boldly stated that if, as in the case of hydrogen chloride, the magnetic rotation and dissociation both increased with dilution, the result proved the truth of the dissociation theory, while equal support to this latter theory was afforded if, as in the case of sulphuric acid, dilution diminished the rotation and increased the dissociation; and the most astonishing part of the argument appeared to be that the nearly double magnetic rotations obtained in some cases should be brought forward as a proof of dissociation, when the observations were made on solutions so strong that the dissociation theory represents them as containing hardly any dissociated substance at all. Surely the natural conclusion to draw from such a doubling when it occurs in the absence of dissociation would be that it could not be explained by dissociation.

2. "The Vapour Density of Ammonium Chloride." By FRANK PULLINGER, B.A., B.Sc., and J. A. GARDNER, B.A.

The authors have made experiments at various temperatures on the vapour density of ammonium chloride. The apparatus used was that of Victor Meyer. In view of the well-known results of Wurtz concerning the vapour

density of phosphorus pentachloride, it was decided to vapourise the ammonium chloride into an atmosphere of ammonia—one of the products of dissociation. In the first instance the experiments were conducted at a moderate red heat, and the salt was vapourised into air. The mean result of five experiments was 0.926; the calculated value for complete dissociation is 0.921.

At 1040° C. (the temperature of boiling zinc), Deville and Troost, using Dumas's method, found the vapour density to be 1.000.

Boiling sulphur was next used, giving a temperature of 448° C. The salt was first vapourised into air. The values found were 0.983 and 0.932. The air was then displaced by ammonia, and the values obtained were 0.939, 0.994, and 1.009.

At a temperature of 360° C. (that of boiling anthracene), the relative density in an atmosphere of air was 0.944, while in an atmosphere of ammonia it was 1.128 and 1.141.

It is evident that in this latter case the ammonium chloride was not wholly dissociated.

It was found impossible to vapourise the salt into ammonia at 300° C. in a bath of boiling α -naphthylamine. In one case, 0.0175 gm. of ammonium chloride was heated for forty minutes, but the loss in weight during that time was only 0.0045 gm., and the volume of ammonia expelled from the apparatus was only 0.91 c.c. In another experiment, 0.0037 gm. was taken, and the loss during forty minutes was 0.0021 gm., no gas being expelled. The vapourisation into air, however, goes on with comparative rapidity at this temperature, and the values found were 0.982, 0.986, and 0.985. The time taken for expulsion of the air was ten to twelve minutes.

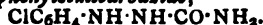
At a temperature of 354° C., Deville and Troost, using a bath of mercury vapour, found that the vapour density was 1.01. The authors propose to continue their experiments at temperatures between 300° and 360°.

3. "Chlorinated Phenylhydrazines." By J. T. HEWITT, B.A., B.Sc.

The author describes the following compounds:—

Orthochlorophenylhydrazine, $\text{ClC}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$, and its hydrochloride.

Orthochlorophenylsemicarbaside,—



Orthochlorophenylphenylsemithiocarbaside,—



Orthochlorophenylhydrazinepyruvic acid,—



Parachlorophenylphenylsemithiocarbaside.

Formylparachlorophenylhydrazine,—



Parachlorophenylhydrazine parabanate,—



Diparachlorophenylurea, $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl})_2$.

The compounds formed by interaction of aldehydes or ketones and orthochlorophenylhydrazine, according to the author, are very unstable.

4. "A New Modification of Phosphorus." By H. M. VERNON, Scholar of Merton College, Oxford.

Observations on the rate of rise of temperature of phosphorus and other experiments have led the author to the conclusion that one or other of two different modifications of phosphorus may result when fused phosphorus solidifies; the new variety is formed when the phosphorus is cooled below its solidifying point and then solidified, and has an undefined melting-point; the ordinary variety of well-defined melting-point being formed when solidification of the phosphorus sets in directly the point of solidification is reached without the temperature sinking below this point. From examination of crystals under the microscope, the author considers that the new variety crystallises in rhombic prisms, the ordinary crystallising in octahedral; he summarises the properties of the two modifications in the following table:—

Octahedral variety.

Has a definite melting-point at 44.3°.

Relative density at 13°, 1.8177.

Has a considerably greater latent heat of fusion than rhombic variety.

Solidifying point, 43.8°.

Rhombic variety.

Has no well-defined melting-point; melts at about 45.3°.

Relative density at 13°, 1.8272

Solidifying point, 43.8°.

DISCUSSION.

Mr. PICKERING thought that Mr. Vernon's conclusions must be accepted at present with great reserve. A difference of 1° in the melting-points, especially where one of these melting-points was undefined, might easily be accounted for by the presence of dissolved matter, accidental impurity, products of oxidation, or some of the oil used to cover the molten phosphorus. Mr. Vernon's curves seem to prove conclusively that this was the case, for that portion which represented the temperature of the substance while it was melting was very much curved, instead of being horizontal as it would be if the phosphorus had been pure. The small difference in the densities—0.01—was equally unsatisfactory, and even if any conclusion could be drawn from a superficial examination of the crystals under the microscope, it would be invalidated by the fact that the specimens examined had both been dissolved in, and re-crystallised from, benzene, for, since fusion had been shown to render the two supposed varieties identical, it was more than probable that dissolution would do the same. It was noticeable that although the two modifications were supposed to be obtained by cooling fused phosphorus, yet the fused phosphorus solidified in each case at the same temperature, a temperature which was not identical with the melting-points of either of the supposed varieties.

Mr. TUTTON concurred with Mr. Pickering in considering that such an important conclusion as to the existence of a new variety of phosphorus was not justified by the data brought forward. It is well known that phosphorus is a substance which exhibits the property of superfusion in a high degree, and the thermal disturbance caused by the sudden solidification of a superfused mass would be likely to influence the results of a determination of melting-point made after solidification under such circumstances. In the speaker's own experiments on the fusion of phosphorous oxide, which also exhibits superfusion in a very marked manner, a determination of melting-point after such solidification from a state of superfusion frequently yielded values differing sometimes by a whole degree from the true melting-point of the substance. It is not at all surprising that a difference of a degree should have been observed by Mr. Vernon, but this fact in itself could scarcely be said to furnish proof of the existence of two modifications. The speaker also took exception to the arbitrary manner in which, from a microscopical examination of which absolutely no details are given, it was concluded that the supposed new modification crystallised in rhombic prisms. Remembering that many really isotropic substances frequently exhibit polarisation colours, owing to their deposition probably in a slight state of strain, it would not be surprising if regular crystals of phosphorus were to exhibit polarisation. It is certainly necessary to have at least data concerning the mode of extinction of the crystals and their behaviour in convergent light before any conclusion can be arrived at as regards their crystalline system.

Means of Recognising the Kind of Size Used in Paper.—W. Herzberg.—Resin-size is evenly distributed in the entire mass of the sheet of paper. Animal size forms two layers entirely separated from each other by the body of the paper. Hence, if the paper is well rubbed and bruised, any characters traced upon it penetrate through if an animal size has been used.—*Mon. Scientifique*.

CORRESPONDENCE.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—We are instructed to ask you to allow the following facts to be made known through your columns to the Fellows of the Chemical Society.

As stated in a former letter, after having carefully considered the suggestions and large number of letters forwarded to us in response to our circular, the following letter was sent by our Committee to the Council of the Chemical Society:—

[COPY.]

4, Lombard Court,
Oct. 31, 1890.

GENTLEMEN,—We are requested, and therefore beg to call your attention to the enclosed circular relating to the present method of electing Fellows of the Chemical Society which has been sent by us to every Fellow resident in the United Kingdom.

A wide-felt opinion as to the necessity of reform led to the issue of this circular, and the answers received thereto shows that it meets with the emphatic support of the Fellows. We therefore trust the subject may receive the immediate and careful attention of the Council.

We are authorised to state that the Council will receive full support in any endeavour they may make to bring about the ends which we have in view. We therefore append from among the additional suggestions which have been sent to us, some which appear worthy of consideration. May we express the hope that you will favour us with an early reply which may be communicated to the Fellows.—We are, &c.,

(Signed) F. J. LLOYD.
F. L. TEED.

Twelve suggestions, additions to those contained in our original circular, were appended to this letter.

On November 6th Professor Thomson formally acknowledged the receipt of this letter, which came before the Council on November 20th. Subsequently, we received the following official reply:—

[COPY.]

Chemical Society, Burlington House,
December 10, 1890.

DEAR SIRS,—The President and Council having under consideration the Memorial addressed to them by you, of date October 31st, would like to be informed who are the body and the individual Fellows by whom you say you are requested to call the attention of the Council to the matters set forth in your Memorial, and are further authorised to state what will be their future contingent action. I shall be obliged if you will please afford me this information, which would obviously be of much weight in guiding the Council to a conclusion on the different matters submitted to them.

Yours faithfully,

(Signed) HENRY E. ARMSTRONG.

Messrs. Lloyd and Teed.

By the instruction of our Committee, the following reply was sent:—

4, Lombard Court,
Dec. 17, 1890.

Henry E. Armstrong, Esq., Ph.D., F.R.S., &c.

DEAR SIR,—In accordance with our letter of the 13th inst., we have laid your communication before the Committee under whose instructions we act, and we are requested to say, in reply, that all Fellows of the Society being equal as to status in the Society, the names of the members of the Committee have nothing to do with the question of the proposed reform in the mode of admission to the Chemical Society.

Further, in view of the very large support which our circular to the Fellows has obtained, we are requested once more to strongly urge upon the Council the necessity of taking the matter in hand immediately.

As to the steps which our Committee and its supporters would take in the future, these certainly depend upon the action of the Council. We have stated, and do so again, that all steps which the Council may take in the direction of reform will be cordially supported by us, our sole aim being the welfare of the Society itself. At the same time, the Committee request us to state that they feel themselves fully strong enough, if necessary, to act without the support of the Council.

(Signed) F. J. LLOYD.
F. L. TEED.

No answer has as yet been received to this letter, and we should therefore be justified in supposing that the Council did not consider it their duty to study the wishes of the Fellows, were it not that the recent number of the *Proceedings*, by containing the names and particulars of the candidates to be balloted for at the next election, shows that our efforts at reform have already had some effect on the Council.

We think it only right that Fellows should be acquainted with our action in the past, that they may form a correct judgment of our action in the future.—We are, &c.,

FREDK. J. LLOYD.
FRANK L. TEED.

London, Feb. 9, 1891.

AN UNSUSPECTED SOURCE OF ERROR.

To the Editor of the Chemical News.

It is usually held by the well-informed, on more or less satisfactory evidence, that there is a special providence charged with the care of midshipmen and fools; but I have never heard the suggestion ventured that chemists enjoy any such privilege of protection. This being so, it all the more behoves us to seize every opportunity of working out our own salvation. The matter about which I am now writing you is a very simple one, and without doubt has come under the notice of most of your readers at some time or other; but since it refers to a danger that might at any time entrap the unwary and lead to a very serious error in analysis, I think it only right to point this out, deeming it probable that I may thus draw the attention of some few readers of the *CHEMICAL NEWS* to a source of error that they might otherwise chance to overlook. Moreover, I think that any danger incident to the use of certain apparatus should not be pointed out once for all, since an occasional repetition of the warning may often meet the eyes of those who have failed to notice an earlier intimation. This is my excuse for troubling you on such a simple matter.

I lately had occasion to determine some saponification equivalents, and proceeded of course in the usual manner, using a conical (Erlenmeyer's) flask in the process. The determination gave me a saponification equivalent of 10.29 per cent KHO. A duplicate in another flask gave me 9.18. This difference was sufficiently disturbing in all conscience; and, in addition, the equivalent was far higher than I had reason to expect it would come. Under these circumstances it was suggested to me by a friend that possibly an error had been introduced by the use of new flasks, owing to a reaction, that is, between the alkali and the silica of the glass. I therefore repeated my determination, using again No. 1 flask, and this time I obtained the saponification equivalent 6.90! A fourth determination in the same flask gave me 6.88—obviously a very close agreement. Under these circumstances, therefore, it seems to me indubitable that in the first two determinations a large quantity of the alkali was used up by reacting with the new glass; after this had taken place the flask was fit for use without fear of any further error.

from such source. The moral, therefore, is obvious: never to trust a saponification result obtained by the use of a new flask.—I am, &c.,

F. H. P. C.

P.S.—It has occurred to me that this warning is the more necessary, since—if I recollect rightly—Mr. Hehner, in his well-known researches on the constitution of beeswax, details a blank experiment made by him to determine whether or no any alkali were consumed by the glass of the flask. He found that none was; but evidently this conclusion must only apply to a seasoned flask, although, of course, I cannot say whether all new flasks would behave as mine did: glass is variable, and some glass may not require such "seasoning."

ALLOYS OF SODIUM AND LEAD.

To the Editor of the Chemical News.

SIR,—Some weeks ago we published a brief note (CHEMICAL NEWS, vol. lxii., p. 314), on some "Alloys of Sodium and Lead" that appear to be definite compounds, giving the observed densities of the alloys and the densities that they should have theoretically as mixtures. In your issue of January 2nd, W. J. A. B. alleges that our calculated densities are erroneous, saying that "the authors give . . . figures which it is difficult to see how they obtain."

Our figures are correct, and it is not difficult to see how W. J. A. B. has blundered. He has calculated for 10, 19.5, and 31.7 volumes of sodium made up to one hundred volumes by lead. We have followed the universal custom of giving analytical results in percentages by weight.

If W. J. A. B. will go over his calculations in the light of this explanation he will doubtless see his error, and we will be glad to see his retraction.—We are, &c.,

GREENE AND WAHL.

Philadelphia, January 30, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiii., No. 3, January 19, 1891.

On the Presence of Sulphur, and on its Part in Vegetation.—MM. Berthelot and André.—Plants take up sulphur incessantly until they flower, the relative proportion of this element being greater by one-third during the first period of vegetation. The sulphur in the state of organic compounds reaches its maximum during inflorescence, and then declines. It seems as if the sulphates derived from the soil were reduced at first and then regenerated after flowering in consequence of an internal oxidation. Still, this supposes that the sulphur is entirely derived from the soil in the state of sulphates, whilst a portion may well be derived directly from organic sulphur-compounds which exist in plenty in the soil. This latter opinion is supported by the fact that organic sulphur is found in quantity in the roots except at the commencement of flowering. Towards the end of flowering it abounds at once in the roots and the stems.

Determination of the Mineral Matters Contained in Vegetable Soils, and on the Part which they Play in Agriculture.—MM. Berthelot and André.—The authors announce that a complete account of their method for determining the constituents of arable soils will be given in a future communication, and they refer to their memoirs in the *Annales de Chimie et de Physique*, Series

6, vol. xv., pp. 86–133; and vol. xiii., p. 74. They affirm that neither the phosphorus nor the total sulphur in a plant or in an arable soil can be determined by the action of acids or by simple incineration. At present they consider chiefly the determination of alkalies and oxides. They effect this, as far as the alkalies are concerned, by a preliminary elimination of the silica by treatment with ammonium fluoride and sulphuric acid, and as for alumina and ferric oxide, by fusion with potassa. The following comparative table shows the results obtained by their exact method, by digestion in the cold with dilute hydrochloric acid, by treatment for several hours with hot concentrated hydrochloric acid, and by treatment with the same acid after incineration. The results refer to 1 kilo:—

	Exact.	Cold HCl.	Hot strong HCl.	Do. after incineration
Potassa ..	8.86	0.21	1.49	1.76
Soda ..	2.11	0.24	0.33	0.42
Magnesia ..	0.87	0.33	—	0.67
Lime ..	11.6	8.79	11.20	10.6
Alumina ..	39.5	1.02	10.09	26.31
Ferric oxide..	21.5	2.96	14.01	16.78

Influence of Solvents upon the Rotatory Power of the Camphols and Iso-camphols: a Study of the Chloral Bornylates.—A. Haller.—The author's results show that, excepting methylic alcohol, the influence of which is manifest, all the other solvents exert no action upon the rotatory power of the lævo-rotatory camphol *a*. The influence of the different liquids upon levo-iso-camphol varies with their function or constitution, but it remains the same for each homologous series.

On the Constitution of the Albumenoids.—Dr. H. Arnaud.—There are three orders of immediate essential principles forming constituent parts of organised matter: hydrocarbons, fatty bodies, and ammonium cyanate. The albumenoids are merely a combination in various proportions of the three immediate principles just enumerated; they contain potentially all three, and it is easy to isolate them. We may consequently consider the albumenoids as true polycyanates of compound ammonia, or of compound polyureas, into the structure of which there enter radicles of hydrocarbons and of fatty acids, replacing the same number of atoms of hydrogen. It may, perhaps, be also admitted that the albumenoids contain in their tissue other radicles still unknown.

Moniteur Scientifique, Queneville.
Series 4, Vol. iv., Part 1.

Determination of Sulphur in Coal.—G. H. Bailey (*Journal of Gas-lighting*).

Analysis of Metallic Tungsten, Tungstic Irons and Steels, and Chromo Irons and Steels.—A. Zeigler (*Dingler*).—This paper will be inserted as early as possible.

Electric Bleaching of Paper.—Two English manufacturers, Evans and Overs, bleach paper electrically, rendering it perfectly white without injury to its strength. The process depends on the use of a solution of magnesium chloride, which is decomposed by the action of a powerful current into chlorine and oxygen on the one hand, and into magnesium and hydrogen on the other. The electrodes are plates of platinum.

Microscopic Examination of Paper.—W. Herzberg.—From the *Zeit. für Anal. Chem.*

New Process for Utilising the Oxygen of the Air.—Georges Kassner (from *Dingler*).—The process turns mainly on the use of the plumbates of the alkaline earths.

Industrial Society of Mulhouse.—Session of April 9, 1890.—The proceedings turned chiefly on the reception and opening of certain "sealed papers."

Revue Universelle des Mines et de la Metallurgie.
Vol. xii., No. 1.

This issue contains no chemical matter.

MEETINGS FOR THE WEEK.

- MONDAY, 16th.**—Medical, 8.30.
Society of Arts, 8. "The Electric Transmission of Power," by Gisbert Kapp.
TUESDAY, 17th.—Institute of Civil Engineers, 8.
Pathological, 8.30.
Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley.
Society of Arts, 4.30. "Chartered Companies in Africa," by Commander V. Lovett Cameron.
WEDNESDAY, 18th.—Society of Arts, 8. "Methods and Processes of the Ordnance Survey," by Colonel Sir Charles Wilson.
Meteorological, 7.
Microscopical, 8.
THURSDAY, 19th.—Royal, 4.30.
Royal Society Club, 6.30.
Institute of Electrical Engineers, 8.
Royal Institution, 3. "The Position of Lull, Purcell, and Scarlatti in the History of the Opera," by Professor C. Hubert H. Parry.
Chemical, 8. Ballot for the Election of Fellows. "On α -Diacetylpentane" and "Synthesis of Dimethyldihydroxyheptanethylenes," by Prof. Perkin and Dr. Kipping.
FRIDAY, 20th.—Royal Institution, 9. "Infectious Diseases, their Nature, Cause, and Mode of Spread," by Edward Emanuel Klein, M.D., F.R.S.
Geological, 3. (Anniversary).
Quekett, 8. (Anniversary).
Society of Arts, 4.30. "The Science of Colour," by Captain Abney.
SATURDAY, 21st.—Royal Institution, 3. "The Forces of Cohesion," by The Right Hon. Lord Rayleigh.

TO CORRESPONDENTS.

G. S. Brewer is advised to read more accurately the passage he professes to criticise.

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THE CHEMICAL NEWS.

VOL. LXIII., No. 1630.

NOTE ON AN IRON CHROMIUM SOIL FROM THE ANDAMAN ISLANDS, EAST INDIES.

By C. J. H. WARDEN,
Chemical Examiner to the Government of Bengal.

THE sample of soil to which the following analysis refers was kindly placed at my disposal by Dr. G. King, F.R.S., C.I.E., Superintendent Royal Botanic Gardens, Calcutta, who had collected it during a recent visit to the Andaman Islands. Few, if any, analyses of soils from these Islands have been made, and but little information is extant in connection with these general physical characters. The only facts I have been able to obtain on these points are recorded by Mr. S. Kurz, a late curator of the Herbarium, Royal Botanic Gardens, Calcutta, in his Report on the vegetation of the Andaman Islands. Mr. Kurz remarks:—"The diversity of soil, considering the smallness of the Islands, is great. Generally, however, the different kinds of soils may be brought under the following heads, which correspond with the three principal formations, viz. :—

"1. The brick coloured soil, extending over the decomposed serpentine rocks.

"2. The yellowish clay, following the sandstone formation, and therefore the most extensive and important kind of soil.

"3. A greyish or blackish soil, characterised by the considerable quantity of siliceous particles it contains, and covering the indurated chloritic or green-stone rock. A black humous soil is predominant in the level valleys, especially along the eastern coasts and on Termoklee Island, where the *kuppalee* trees—*Mimusops Indica*—grow beautifully."

Mr. Kurz further adds:—"According to the greater or smaller amount of moisture, these different kinds of soil are more or less mingled with decayed vegetable matter, and accordingly are more or less fertile." Mr. Kurz also states that "oxide of iron is indicated everywhere by the rusty colour of some sandstones and other rocks, and iron pyrites not unfrequently occur in the chloritic and serpentine rocks."

The sample of soil received from Dr. King had been collected from the plantation of Liberian Coffee, and was of a chocolate colour, probably corresponding with the "brick coloured soil" of Mr. Kurz's classification. On mechanical analysis, the following results were obtained:—

	Fixed substances.	Combustible or volatile matter.
0.191 { Gravel retained by a sieve with 30 meshes to the linear inch	0.167	
0.168 { Organic matter		0.024
0.168 { Gravel retained by 50 meshes	0.148	
0.168 { Organic matter		0.020
57.980 { By elutriation, coarse sand	49.520	
57.980 { Organic matter		8.460
41.661 { Fine sand and soil	37.201	
41.661 { Organic matter		4.460
100.000	87.036	12.964

Stones retained by a sieve with 18 meshes 0.57 per cent.
Organic matter, consisting of bits of stick, fragments of leaves, &c. .. 0.004 ..

The largest fragment of mineral separated weighed only 0.2 grm.

The following determinations of the physical properties of the soil were made:—

The specific gravity was 3.06, calculated on the dry soil, water at 15.5° C. being taken as unity.

The Porosity.—61 per cent by volume of the soil was found to be capable of being occupied by air.

Absolute Weight.—One cubic foot of the air-dried soil, containing 11.341 per cent of moisture, weighed 429,300 grms.

Capacity for Water.—When saturated with water, the soil was found capable of holding 52.6 per cent.

Evaporation of Moisture.—The soil saturated with moisture lost on exposure to air—

After 21 hours 10 mins. exposure		18.0 per cent.
" 45 " 10 " "		33.5 "
" 69 " 30 " "		43.6 "

These results may also be stated in a different way:—

The saturated soil retained after exposure to air for—

21 hours 10 mins.	34.6 per cent of moisture.
45 " 10 "	19.0 " "
69 " 30 "	9.0 " "

In these experiments the dry bulb thermometer varied between 88°—89° F., and the wet bulb 83°—84° F.

The absorptive power of the soil in an atmosphere saturated with moisture, the temperature being 83°—89° F., was as follows:—The soil dried at 100° C. took up in eleven days 20.801 per cent of moisture.

On chemical analysis the following results were obtained, which have been calculated on the air-dried soil. The reaction of the soil was acid, and was not due to CO₂.

Moisture lost at 100° C.	11.3410
Anhydrous humus	
Calculated from organic carbon	10.4459
Loss on ignition, 12.9640 per cent.	
Organic carbon, 2.5643 per cent.	
Nitrogen as nitric acid	0.00129
Organic nitrogen and ammonia	0.24080
Chemically combined water, not evolved at 100° C.	2.27730
CaO	0.2941
Fe ₂ O ₃	35.4326
Al ₂ O ₃	10.4914
MgO	0.1094
Traces of chromium	—
Mn ₂ O ₄	0.4174
Na ₂ O	0.4554
K ₂ O	0.8633
Cl	0.0061
P ₂ O ₅	0.4004
SO ₃	0.1386
Traces of CO ₂	—
SiO ₂	0.0455

Containing—
SiO₂ .. 12.3681
Al₂O₃ .. 0.0776
Residue from HCl, soluble in alkalies 14.4819

Containing—
Fe₂O₃
Al₂O₃
Cr₂O₃
Residue insoluble in alkalies, decomposable by concentrated H₂SO₄ 2.6569

CaO .. 0.1212
MgO .. 0.1107
Residue not decomposable by H₂SO₄, containing sand, iron, and chromium in traces .. 9.2558

100.35509

The total amount of chromium present in the soil calculated as Cr₂O₃ was 1.6139 per cent. It will be of interest to ascertain whether the ash of coffee plants grown on this soil contains any trace of chromium or not.

NOTE ON THE ESTIMATION OF GREASE.

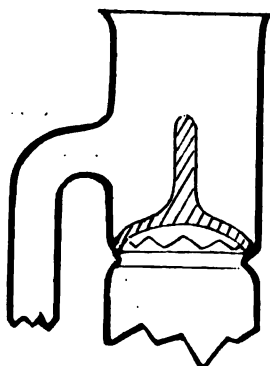
By W. LAWRENCE GADD F.I.C., and S. LEES, F.C.S.

THE authors have devised a simple modification of the ordinary Soxhlet tube for fat extraction, when used for extracting very light or finely-powdered substances, which gives excellent results in their hands, and which, they believe, may be of service to other chemists under similar circumstances.

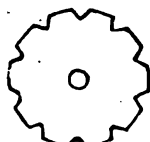
The samples under examination were very fine, floury deposits, which, when agitated even slightly with the ether employed for their extraction, were thrown up into suspension and subsided again only very slowly; and one sample was so light that great care was necessary in handling the weighed quantities, as a slight motion was sufficient to cause clouds of dust to arise from the substance.

As the samples, when treated with ether, passed entirely through both glass and cotton-wool plugs placed at the bottom of the Soxhlet tube, the weighed quantity for each estimation was carefully placed in an ordinary star filter, previously extracted with ether, and the filter and its contents pushed down the tube until it rested on the plug of glass-wool at the bottom.

The modified tube used was specially made with an annular projecting inside ring, on which rested an inverted glass cup, provided with a short stem to facilitate removal, and having cut in its periphery a number of channels or grooves, as shown in the sketch.



SECTION



PLAN

The down rush of ether from the condenser, when the syphoning action took place, was received by this glass cup, and, passing through the channels above mentioned, flowed quietly down the sides of the tube without in the least disturbing the material in the filter, which was rapidly and thoroughly extracted without any of the powder passing into the tared flask; whilst previous attempts to use the ordinary extractor had resulted in the whole of the material being speedily washed out of the filter and finding its way into the weighed flask.

The authors have repeatedly used their modified tube

for extracting a variety of substances, with very satisfactory results, and they believe it can be made without adding materially to the cost of the ordinary Soxhlet extractor.

Chemical Laboratory and Assay Office,
55 and 56 Barton Arcade, Manchester, February, 1891.

THE USE OF DRY REACTIONS IN
QUALITATIVE ANALYSIS.

By W. TATE, Assoc.R.C.S.

THE accompanying table was drawn up by the author to facilitate and systematise the use of the more characteristic dry reactions in qualitative analysis. Use with large classes has shown that these tests can be most advantageously applied to the separated group precipitates, as time is economised by this method.

The tests given have been culled from various sources, and modified as required by the characters of the precipitates to be tested.

Table of Dry Reactions.

The group precipitates may be tested during the operation of washing by the reactions arranged in this table, the adhering mother-liquor not affecting the results.

GROUP I.

Precipitate may contain AgCl , Hg_2Cl_2 , PbCl_2 . If lead be present it is preferable not to examine for silver in the dry way.

1. Take up a minute portion of the precipitate on an asbestos thread,* and hold it in the upper reducing flame of a Bunsen burner. Support an evaporating basin, nearly filled with water, a little above the thread.

A grey sublimate on the bottom of the dish indicates *mercury*. This sublimate, on exposure to the fumes of HI ,† becomes brilliantly coloured, streaky red and yellow, from formation of HgI_2 .

2. Heat a small portion of the precipitate on charcoal till the Hg_2Cl_2 has been driven off. If there be a residue add to it a mixture of KI and sulphur, and heat strongly; a yellow incrustation indicates *lead*.
3. If lead be absent fuse a portion of the precipitate with Na_2CO_3 on charcoal.

A white malleable metallic bead not marking paper indicates *silver*.

GROUP II.—Copper Sub-Group.

Residue of sulphides after digestion with NaOH ; it may contain CuS , CdS , Bi_2S_3 , PbS , HgS .

4. Drive off HgS on charcoal, and heat the residue with $\text{KI} + \text{S}$. (See 2.) A fine red to reddish-brown incrustation indicates *bismuth*, yellow *lead*.

If bismuth be present the lead incrustation may be masked, though the presence of both metals may be recognised with practice.

5. Asbestos thread sublimate in R.F. (See 1.)

Grey sublimate indicates *mercury*; confirm as before. A brownish-black sublimate nearer the centre of the dish indicates Bi , Pb , or Cd .

6. Heat a portion of the precipitate in a closed tube with Na_2CO_3 and KCy .

A grey metallic mirror, rubbing into minute globules when stroked with a match, indicates *mercury*.

7. Make a clear borax bead, add a little of the precipitate, and fuse in the oxidising flame of the Bunsen burner.

* The asbestos thread may be wrapped round the end of an iron wire.

† Most readily, by saturating an asbestos plug with a strong alcoholic solution of iodine, igniting the alcohol, and holding the flame beneath the basin.

Green to blue bead indicates *copper*; confirm by adding a trace of a tin salt, and holding in R.F. for one minute; a red opaque bead indicates copper.

Arsenic Sub-Group.

Sulphides precipitate from NaOH solution on addition of HCl and passage of a few bubbles of H_2S ; it may contain As_2S_3 , Sb_2S_3 , and SnS or SnS_2 .

8. Colour a borax bead faintly with Cu, hold in R.F. of Bunsen burner for one minute; the bead should remain clear blue. Add a trace of the sulphides precipitate, oxidise till the bead is once more clear blue, and then hold in R.F. for one minute.

An opaque red bead indicates *tin*.

9. Sublimate (from asbestos) on porcelain in R.F. (See 1.)

Sublimate is black and soluble in solution of NaOCl, *arsenic*. Sublimate is black and insoluble in solution of NaOCl, *antimony*. If both antimony and arsenic be present the stain will be dissolved round the edges.

10. Obtain sublimate as in 1, but hold thread in the oxidising flame, and the porcelain basin some little distance above the flame.

A white sublimate of oxides almost invisible on the porcelain is obtained.

Touch the sublimate with one drop of $AgNO_3$ solution, and expose the moistened spot to the gas evolved from strong solution of ammonia.

If the moistened sublimate blackens, *antimony* is present; a yellow or yellowish-red stain indicates *arsenic*. (Both may often be distinguished together.)

The black stain is insoluble, the yellow stain soluble, in ammonia solution.

11. Dry a small portion of the precipitate, mix it with twice its bulk of SiO_2 and a little dry sodium acetate; heat the mixture (in a fume chamber), in a tube closed at one end, placing a finger over the open end of the tube. If the finger, on removal, possesses the characteristic and disgusting odour of cacodyl, *arsenic* is present.

GROUP III.—*Iron Sub-Group.*

There may be present $Fe_2(OH)_6$, $Al_2(OH)_6$, $Cr_2(OH)_6$.

12. Borax bead in O.F.

Yellowish red bead indicates *iron*.

Bright green bead indicates *chromium*.

Brown olive-green bead would be caused by Fe together with Cr.

13. Fuse a part of precipitate with Na_2CO_3 and KNO_3 on a piece of platinum foil.

A yellow mass indicates *chromium*. (Green, Mn partly precipitated here.)

14. If 12 and 13 give no colour tests, and the precipitate be white, heat a portion strongly on charcoal, moisten with cobalt nitrate solution, and again heat strongly before the blowpipe.

Blue earthy (not glassy) mass proves the presence of *aluminium*.

Zinc Sub-Group.

The precipitate may contain ZnS , MnS , CoS , NiS .

15. Borax bead in O.F.

Blue, *cobalt*; reddish brown, *nickel*.

16. Fuse with Na_2CO_3 and KNO_3 on clean platinum foil. A green mass indicates *manganese*.

17. If CO and Ni be absent, test, as in 14, with $CO(NO_3)_2$ on charcoal.

A green mass indicates *zinc*.

GROUP IV.

The precipitate may contain $BaCO_3$, $SrCO_3$, $CaCO_3$.

18. Take up a minute portion of the precipitate on platinum wire, moisten with HCl, and hold wire in Bunsen flame.

The flame is coloured green for *barium*, crimson for *strontium*, brick-red for *calcium*.

GROUP V.

19. Flame reaction as in 18.

Flame is brilliantly yellow, *sodium*; flame is violet, *potassium*.

If sodium be present view the flame through an indigo prism; the violet potassium flame may then be distinguished, but is not to be much relied on.

THE PHOTOGRAPHY OF COLOURS.

By G. LIPPMANN

THE author undertook to obtain upon a photographic plate the image of the spectrum, with its colours, so that the image should remain afterwards fixed and might be indefinitely exposed to full daylight without change.

He has been able to solve the problem by operating with the sensitive materials, the developers, and the fixing agents currently used in photography, and merely modifying the physical conditions of the experiment.

The essential conditions for obtaining colours in photography are the continuity of the sensitive layer and the presence of a reflecting surface behind this layer. By continuity is to be understood the absence of granules. The silver iodide, bromide, &c., must be disseminated within a film of albumen, gelatin, or some other transparent or inert material in a uniform manner, and without forming granules visible even under the microscope. If there are any particles they must be of dimensions which may be neglected in comparison to the length of a luminous wave.

The use of the coarse emulsions used at present is therefore excluded. A continuous layer is transparent, save generally for a slight blue opalescence. The author uses as support albumen, collodion, and gelatin; as sensitive matters, silver iodide and bromide. All these combinations give good results.

The plate, when dry, is supported by a hollow frame into which mercury is poured; this mercury forms a reflecting layer in contact with the sensitive film. The exposure, the developing, and the fixation are done as if it were intended to obtain a black negative of the spectrum, but the result is different. When the proof is finished and dried the colours appear.

The proof obtained is negative by transmitted light; that is to say, that each colour is represented by its complementary. By reflected light it is positive, and we see the colour itself which may be obtained very brilliant. To obtain in this manner a positive, the impression must be strengthened in such a manner that the photographic deposit has a bright colour, which is obtained by the use of acid liquids.

The fixation is effected by means of hyposulphite, followed by careful washings. The author has ascertained that the colours then resist the most intense electric light.

The theory of the experiment is very simple. The incident light which forms the image in the camera interferes with the light reflected by the mercury. There is consequently formed in the interior of the sensitive film a system of fringes, i.e., of luminous maxima and dark minima. The maxima alone act upon the plate; at the close of the photographic operations these maxima remain masked by deposits of silver, more or less reflective, which occupy their place. The sensitive layer is divided by these deposits into a series of thin laminæ, the thickness of which is the interval which separates two maxima; that is to say, a half wave-length of the incident light. These slender laminæ have, therefore, precisely the thickness necessary to reproduce the incident wave-length by reflection.

The colours visible upon the proof are exactly of the same nature as those of soap bubbles. They are even more pure and brilliant, at least if the photographic operations have yielded a deposit which reflects well. In this case there are formed in the thickness of the sensitive film a very great number of superimposed slender films; about 200 if the film, e.g., is $\frac{1}{16}$ in thickness. For the same reason, the reflected colour is so much the purer as the number of reflecting films is increased. These layers form in fact a sort of screen in depth, and for the same reason, that in the theory of screens by reflection the purity of the colours increases with the number of elementary mirrors.—*Comptes Rendus*, cxii., p. 274.

ON THE CURIOUS BEHAVIOUR OF CERTAIN ZINC- SULPHIDE COMPOUNDS.

By JOHN CAWLEY,
Associate Royal School of Mines, England.

SOME years ago I promised to send to the *CHEMICAL NEWS* a communication on the subject named in the heading of this article. Important business considerations prevented my fulfilling the promise at that time; I do not think, however, it is too late to do so now should the Editor deem the matter of sufficient interest to occupy his valuable space.

My long experience as a manufacturer of colours enables me to speak very positively respecting the industrial importance of this subject. Unfortunately, the experiments herein recorded, and many hundred others not so recorded, were made in the midst of considerable business worry; they were consequently not always well considered, and worse than all, lead to no very well-defined conclusions. They may, however, suggest to some ambitious young chemist an interesting and not unprofitable line of research. It will make what follows more intelligible if I give here a brief description of the method generally employed in preparing zinc-sulphide pigments.

Zinc sulphate, or chloride freed from iron, manganese, lead, tin, &c., is precipitated by an alkaline or alkaline-earthly sulphide; the precipitate consisting of hydrated zinc-sulphide alone or in admixture with a sulphate of an alkaline earth, is dried and ignited at a red heat; the red-hot product is thrown into water, levigated, washed, dried again, and reduced to fine powder. The pigment is then ready for grinding in oil as a paint.

This process, simple in outline, requires considerable skill and experience to carry it out successfully, but if well carried out it produces a pigment superior to the best white-lead in respect of whiteness, body, and covering power. It is, moreover, relatively innocuous, and is not discoloured by gases containing SH_2 .

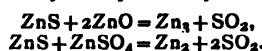
In general, however, it is subject to the grave defect of darkening when exposed to sunlight, the darkening apparently being due not only to light, but also dependent on the condition of the atmosphere, in respect of moisture-contents, &c. I have prepared pigments so sensitive as to be turned almost black when exposed to bright sunlight for one or two minutes. A curious thing to be noted in this connection is that the darkened pigment will completely regain its whiteness when placed in the dark for a few hours, and when so bleached it appears to be somewhat less sensitive than it was originally. It would be too long a story to go into all the details of experiments made by me in connection with this matter. I will therefore content myself by giving a brief account of the more important observations, interpolating here and there remarks of an explanatory character.

1. The dried hydrated zinc-sulphide, before ignition, is not altered by exposure to light; after ignition it darkens readily.

2. The whitest and purest zinc blende obtainable was levigated and exposed to light. No darkening was observed, but the same blend, calcined so as to slightly oxidise it, was readily darkened.

3. Zinc-sulphide was prepared in a very finely-divided condition and free from hydration, by burning zinc in an atmosphere of sulphur vapour, and collecting the product in a chamber, the temperature of which was high enough to prevent the condensation of sulphur. This sulphide was unchanged by light, but like the blende, darkened readily after slight calcination.

In connection with the observations above named, I may say I had been struck by the resemblance which the colour developed in the pigment by light bore to that of the finely-divided metal deposited from certain metallic solutions. I found, too, as might have been expected, that in the ignition of hydrated zinc-sulphide, even when air is excluded, oxidised zinc compounds are always formed, and in this way the idea was suggested to me that light might be able, under certain conditions, to effect the reactions which, as is well known, heat does. These reactions may be expressed by the equations—



According to this hypothesis the darkening is due to the formation of a film of metallic zinc, which, owing to its finely-divided condition, would readily oxidise in the absence of light; the bleached pigment would therefore be less sensitive than it was originally, as it would be protected somewhat by a film of non-sensitive zinc oxide. This theory explained easily all the observed facts for a time, but was afterwards found to be untenable.

4. Noting that the pigment moistened with water was more sensitive than when in a dry condition, a sample was dried at 120°C ., and, while warm, was placed in a glass tube which was sealed before the blowpipe. Result—no discolouration after one year's exposure. A sample placed in a sealed tube without extra drying was readily darkened.

An attempt was made to practically apply this observation by thoroughly drying the pigment *immediately before* grinding in linseed oil, the latter being as free from water as possible, the idea being that the oil would exercise a protective effect similar to that of the sealed tube. Result not satisfactory.

5. Taking a sample of pigment not very sensitive, *per se*, it was noted that its sensitiveness was enormously increased by moistening it with a weak solution of zinc sulphate, from which it was inferred that the sensitiveness might be due to imperfect washing. The most thorough washing, however, would not remove the basic zinc sulphate formed in the process of ignition.

6. Attempts were made to decompose this basic sulphate into zinc oxide, and an inert sulphate by treating the pigment with solutions of the hydrates of potassium, sodium, barium, and calcium; the first three were rejected, as they appeared to act on the zinc-sulphide itself. Lime-water exercised for a short time a decidedly protective effect; afterwards it seemed to lose its power of making the pigment resistant to light.

The best results were obtained by mixing with the zinc-sulphide precipitate about one-half of 1 per cent of *freshly precipitated* magnesium hydrate. The resulting pigment was fairly resistant to light, but the presence of magnesium somewhat impaired its general qualities. In this connection I may remark that I have noticed a certain amount of incompatibility as regards zinc-sulphide pigments between the quality of light resistance and other desirable qualities, such as extreme whiteness, softness, and opacity. In igniting hydrated sulphide of zinc, even when the utmost care is used, it is almost impossible to avoid a certain amount of fritting of the particles of the substance; and when this is excessive the pigment is worthless, as it becomes yellow, stony, and wanting in opacity. This tendency to fritting was overcome by

mixing the dried precipitate, before ignition, with about 5 per cent of common salt. The latter, at the temperature of the furnace, fuses and appears to form a glaze round the particles of the pigment. This glaze immediately dissolves when the red-hot pigment is thrown into water, and the product resolves itself into a soft mass of great whiteness and opacity. Unfortunately, the product so obtained, while excellent in most respects, is extremely sensitive to light.

After several years' experience I succeeded in manufacturing on a large scale a pigment which stood the severest tests of exposure to light under all sorts of atmospheric conditions, but the process was a little uncertain, as one or two batches, for some unknown reason, were more or less sensitive.

The improved process was conducted as follows:—The zinc-salt and barium sulphide were made as concentrated as was practicable, the sulphide being used at a boiling temperature. The precipitate formed, consisting mainly of zinc-sulphide and sulphate of barium in equivalent proportions, was very readily filterable. To the vat containing the precipitate was added one half of 1 per cent of magnesium hydrate freshly made, and an amount of common salt in fine powder. The filtration carried away considerable quantities of the salt added, but enough remained to produce the anti-fritting effect above mentioned. The waste of salt was a trifling matter in comparison with the convenience of getting perfect admixture with a minimum of labour. The precipitate, after drying, was crushed to the size of small beans and mixed with 3 per cent ammonium chloride before ignition.

The way in which the ammonium chloride acts I do not attempt to explain, nor do I know why in a few instances the above mentioned failed to produce a stable pigment.

About the time we had fairly perfected our process, a combination of business circumstances made it expedient for us to abandon the manufacture. Since that time I have had little opportunity of giving the matter any attention, though I have often had it in my mind to call the attention of readers of the CHEMICAL NEWS to a phenomenon which, as far as I am aware, is little known, and has never been scientifically investigated. I am not without hope that I may be able in the near future to make a systematic investigation of it myself; in the meantime I trust this brief account may not be found quite uninteresting.

278, Passaic Street, Newark, N.J.,
Jan. 28, 1891.

Electro-Metallurgy of Aluminium.—Adolphe Minet. —Recent researches on the electrolysis of aluminium fluoride in a state of fusion have enabled the author to increase the yield of the system. He has succeeded in producing 32 grms. of metal by the expenditure of a quantity of energy equivalent to 1 horse-power. The losses, however, are still 30 per cent.—*Comptes Rendus*, vol. cxii., No. 4.

Chemical Theory of the Coagulation of Blood.—M.M. Maurice Arthus and Calixte Pagès.—The author's experiments complement the theories of Alexander Schmidt and Hammarsten by showing the fibrinoplastic action of the salts of calcium. If we receive 225 c.c. of blood in 25 c.c. of a solution of potassium oxalate at 0.9 per cent, the blood will not coagulate spontaneously, whatever is the temperature or the time of action. For the potassium oxalate there may be substituted the corresponding sodium or ammonium salts, or a fluoride, a silicate, or an alkaline soap. These substances may be employed either in strong or weak solution or in fine powder. On the other hand the subsequent addition to the blood of a solution of calcium chloride restores its coagulating power.—*Comptes Rendus*, vol. cxii., No. 4.

ELECTRICITY IN TRANSITU: FROM PLENUM TO VACUUM.*

By WILLIAM CROOKES, F.R.S.,
President of the Institution of Electrical Engineers
(Continued from p. 80).

Properties of Radiant Matter.

ONE of the most characteristic attributes of Radiant Matter—whence its name—is that it moves in approxi-

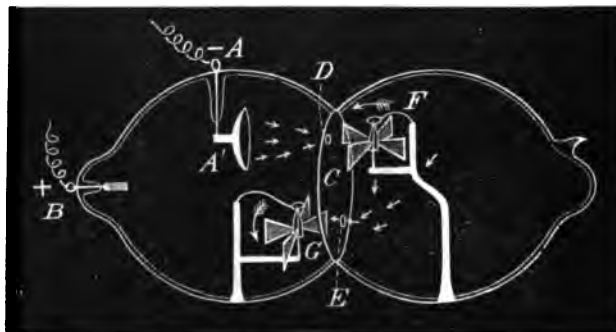


FIG. 14.—P. = 0.001 m.m., or 1.3 M.

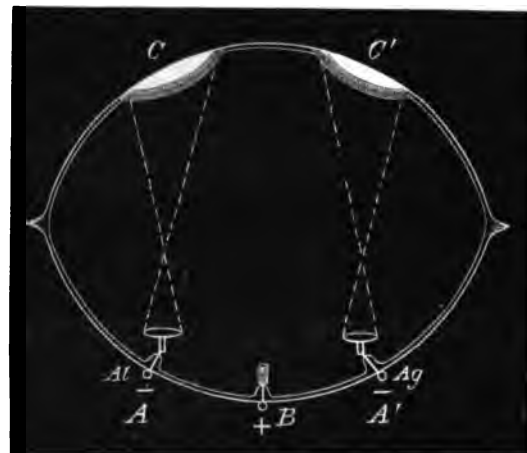


FIG. 15.—P. = 0.00068 m.m., or 0.9 M.

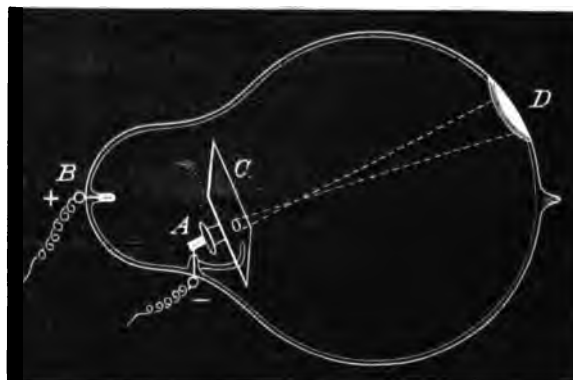


FIG. 16.—P. = 0.00068 m.m., or 0.9 M.

* Inaugural Address delivered January 15th, 1891.



FIG. 17.—P. = 2 m.m.

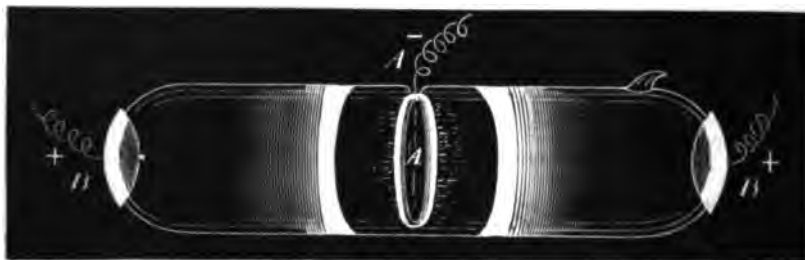


FIG. 18.—P. = 0.076 m.m., or 100 M.



FIG. 19.—P. = 0.00068 m.m., or 0.9 M.

mately straight lines and in a direction almost normal to the surface of the electrode. If we keep the induction current passing continuously through a vacuum tube in the same direction, we can imagine two ways in which the action proceeds; either the supply of gaseous molecules at the surface of the negative pole must run short, and the phenomena come to an end, or the molecules must find some means of getting back. I will show you an experiment which reveals the molecules in the very act of returning. Here is a tube (Fig. 14) exhausted to a pressure of 0.001 m.m., or 1.3 M. In the middle of the tube is a thin glass diaphragm, C, pierced with two holes, D and E. At one part of the tube a concave pole, A', is focussed on the upper hole, D, in the diaphragm. Behind the upper hole and in front of the lower one are movable vanes, F and G, capable of rotation by the slightest current of gas through the holes.

On passing the current with the concave pole negative, the small vanes rotate, in such a manner as to prove that at this high exhaustion a stream of molecules issues from the lower hole in the diaphragm, whilst at the same time a stream of freshly charged molecules is forced by the negative pole through the upper hole. The experiment speaks for itself, showing as forcibly as an experiment can show that so far the theory is right.

This view of the ultra-gaseous state of matter is advanced merely as a working hypothesis, which, in the present state of our knowledge, may be regarded as a necessary help to be retained only so long as it proves useful. In experimental research early hypotheses have necessarily to be modified, or adjusted, or perhaps entirely abandoned, in deference to more accurate observations. Dumas said, truly, that hypotheses were like crutches which we throw away when we are able to walk without them.

Radiant Matter and "Radiant Electrode Matter."

In recording my investigations on the subject of radiant matter and the state of gaseous residues in high vacua under electrical strain, I must refer to certain attacks on the views I have propounded. The most important of

by Puluj on "Radiant Electrode Matter and the So-called Fourth State." Dr. Puluj's paper concerns me most, as the author has set himself vigorously to the task of

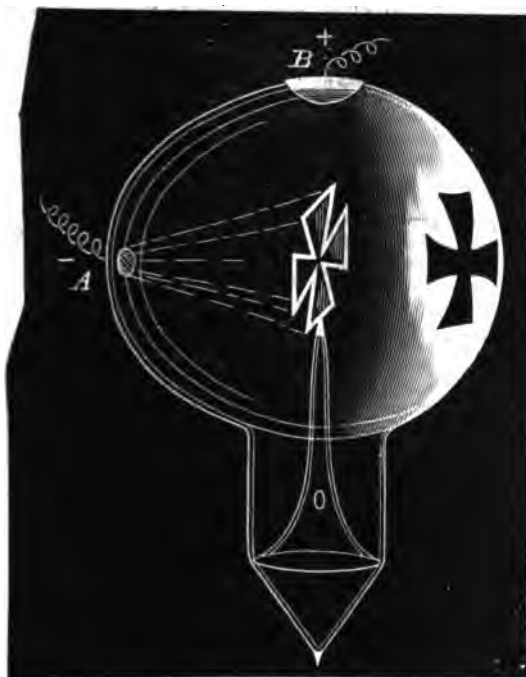


FIG. 20.— $P = 0.00068$ m.m., or 0.9 M.

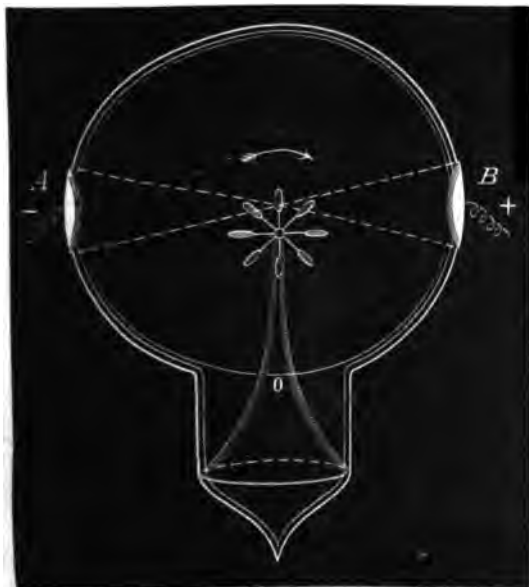


FIG. 21.— $P = 0.001$ m.m., or 1.3 M.

these questionings are contained in a volume of "Physical Memoirs," selected and translated from foreign sources under the direction of the Physical Society (vol. i., Part 2). This volume contains two memoirs, one by Hittorff on the "Conduction of Electricity in Gases," and the other

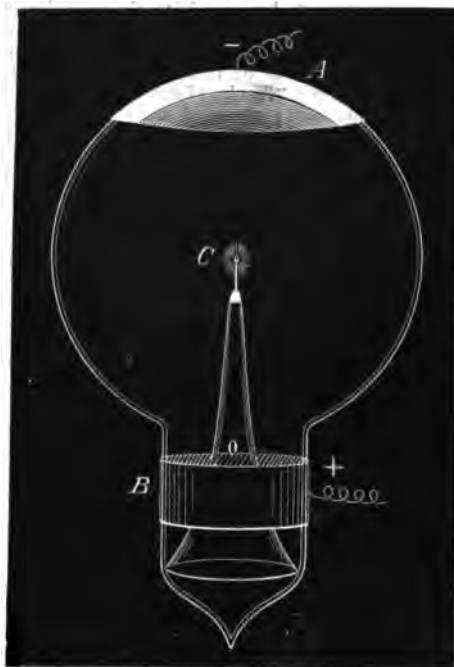


FIG. 22. $P = 0.000076$ m.m., or 0.1 M.

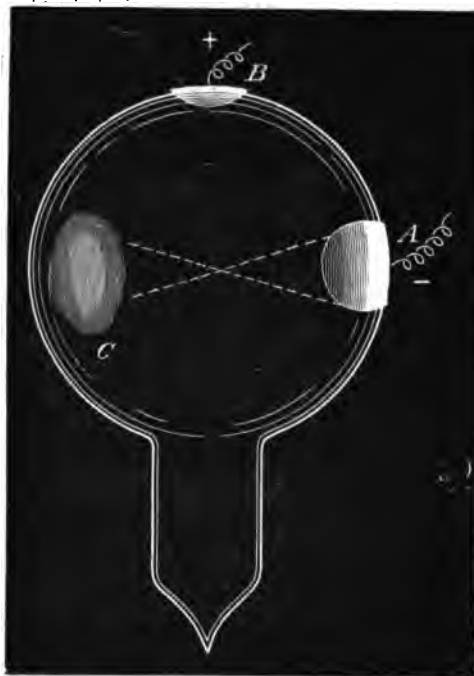


FIG. 23.— $P = 0.00068$ m.m., or 0.9 M.

opposing my conclusions. Apart from my desire to keep controversial matter out of an address of this sort, time would not permit me to discuss the points raised by my

critic. I will therefore only observe in passing that Dr. Puluj has no authority for linking my theory of the fourth state of matter with the highly transcendental doctrine of four dimensional space.

Reference has already been made to the mistaken supposition that I have pronounced the thickness of the dark space in a highly-exhausted tube, through which an induction spark is passed, to be identical with the natural mean free path of the molecules of gas at that exhaustion. I could quote numerous passages from my writings to show that what I meant and said was the mean free path as amplified and modified by the electrification.* In this view I am supported by Professor Schuster,† who in a passage quoted below distinctly admits that the mean free path of an electrified molecule may differ from that of one in its ordinary state.

The great difference between Puluj and me lies in his statement that‡ "the matter which fills the dark space consists of mechanically detached particles of the electrodes which are charged with statical negative electricity, and move progressively in a straight direction."

To these mechanically detached particles of the electrodes, "of different sizes, often large lumps,"§ Puluj attributes all the phenomena of heat, force, and phosphorescence that I from time to time have described in my several papers.

Puluj objects energetically to my definition "Radiant Matter," and then proposes in its stead the misleading term, "Radiant Electrode Matter." I say "misleading," for while both his and my definitions equally admit the existence of "Radiant Matter," he drags in the hypothesis that the radiant matter is actually the disintegrated material of the poles.

Puluj declares that the phenomena I have described in high vacua are produced by his irregularly shaped lumps of Radiant Electrode Matter. My contention is that they are produced by Radiant Matter of the residual molecules of gas.

Were it not that in this case we can turn to experimental evidence I would not mention the subject to you. On such an occasion as this controversial matter must have no place; therefore I content myself, at present, by showing a few novel experiments which demonstratively prove my case.

Let me first deal with the Radiant Electrode hypothesis. Some metals, it is well known, such as silver, gold, or platinum, when used for the negative electrode in a vacuum tube, volatilise more or less rapidly, coating any

object in their neighbourhood with a very even film. On this depends the well-known method of electrically preparing small mirrors, &c. Aluminium, however, seems exempt from this volatility. Hence, and for other reasons, it is generally used for electrodes.

If, then, the phenomena in a high vacuum are due to the "electrode matter," the more volatile the metal used the greater should be the effect.*

Here is a tube (Fig. 15, P. = 0.00068 m.m., or 0.9 M.), with two negative electrodes, A, A', so placed as to project two luminous spots on the phosphorescent glass of the tube. One electrode, A', is of pure silver, a volatile metal, the other, A, is of aluminium, practically non-volatile. A quantity of "electrode matter" will be shot off from the silver pole, and practically none from the aluminium pole; but you see that in each case the phosphorescence, c, c', is identical. Had the Radiant Electrode Matter been the active agent the more intense phosphorescence would proceed from the more volatile pole.

A drawing of another experimental piece of apparatus is shown in Fig. 16. A pear-shaped bulb of German glass, has near the small end an inner concave negative pole, A, of pure silver, so mounted that its inverted image is thrown upon the opposite end of the tube. In front of this pole is a screen of mica, c, having a small hole in the centre, so that only a narrow pencil of rays from the silver pole can pass through, forming a bright spot, d, at the far end of the bulb. The exhaustion is about the same as in the previous tube, and the current has been allowed to pass continuously for many hours so as to drive off a certain portion of the silver electrode, and upon examination it is found that the silver has all been deposited in the immediate neighbourhood of the pole, whilst the spot, d, at the far end of the tube that has been continuously glowing with phosphorescent light is practically free from silver.

The experiment is too lengthy for me to repeat it here, so I shall not attempt it, but I have on the table the results for examination.

The identity of action of silver and aluminium in the first case, and the non-projection of silver in this second instance, in themselves are sufficient to condemn Dr. Puluj's hypothesis, since they prove that phosphorescence is independent of the material of the negative electrode. In front of me is a set of tubes that to my mind puts the matter wholly beyond doubt. The tubes contain no inside electrodes with the residual gaseous molecules, and with them I will proceed to give some of the most striking radiant matter experiments without any inner metallic poles at all.

In all these tubes the electrodes, which are of silver, are on the outside, the current acting through the body of the glass. The first tube contains gas only slightly rarefied and at the stratification stage. It is simply a closed glass cylinder, with a coat of silver deposited outside at each end, and exhausted to a pressure of 2 m.m. The outline of the tube is shown in Fig. 17. I pass a current and, as you see, the stratifications, though faint, are perfectly formed.

The next tube, seen in outline in Fig. 18, shows the dark space. Like the first it is a closed cylinder of glass, with a central indentation forming a kind of hanging pocket, and almost dividing the tube into two compartments. This pocket, silvered on the air side, forms a hollow glass diaphragm that can be connected electrically from the outside, forming the negative pole, A; the two ends of the tube, also outwardly silvered, form the positive poles, B, B. I pass the current and you all see the dark space distinctly visible. The pressure here is 0.076 m.m., or 100 M.

The next stage, dealing with more rarefied matter, is

* "The thickness of the dark space surrounding the negative pole is the measure of the mean length of the path of the gaseous molecules between successive collisions. The electrified molecules are projected from the negative pole with enormous velocity, varying however with the degree of exhaustion and intensity of the induction current."—(Phil. Trans., Part I., 1879, par. 530).

† "The extra velocity with which the molecules rebound from the excited negative pole keeps back the more slowly moving molecules which are advancing towards the pole. The conflict occurs at the boundary of the dark space, where the luminous margin bears witness to the energy of the discharge."—(Phil. Trans., Part I., 1879, par. 507).

‡ "Here, then, we see the induction spark actually illuminating the lines of molecular pressure caused by the excitement of the negative pole."—(R. I. Lecture, Friday, April 4th, 1879).

§ "The electrically excited negative pole supplies the force majeure which entirely, or partially, changes into a rectilinear action the irregular vibration in all directions."—(Proc. Roy. Soc., 1880, page 472).

"It is also probable that the absolute velocity of the molecules is increased so as to make the mean velocity with which they leave the negative pole greater than that of ordinary gaseous molecules."—(Phil. Trans., Part II., 1881, par. 719).

† "It has been suggested that the extent of the dark space represents the mean free path of the molecules. . . . It has been pointed out by others that the extent of the dark space is really considerably greater than the mean free path of the molecules, calculated according to the ordinary way. My measurements make it nearly twenty times as great. This, however, is not in itself a fatal objection; for, as we have seen, the mean free path of an ion may be different from that of a molecule moving among others."—Schuster, Proc. Roy. Soc., xlvii., pp. 556-7.

‡ "Physical Memoirs," Part II., vol. 1, page 244. The paragraph is italicised in the original.

§ Loc cit. p. 242.

* In a valuable paper read before the Royal Society, November 20th, 1890, by Professors Livinge and Dewar, on finely-divided metallic dust thrown off the surface of various electrodes in vacuum tubes, they find not only that dust, however fine, suspended in a gas will not act like gaseous matter in becoming luminous with its characteristic spectrum in an electric discharge, but that it is driven with extraordinary rapidity out of the course of the discharge.

that of phosphorescence. Here is an egg-shaped bulb, shown in Fig. 19, containing some pure yttria, and a few rough rubies. The positive electrode, B, is on the bottom of the tube under the phosphorescent material; the negative, A, is on the upper part of the tube. See how well the rubies and yttria phosphoresce under molecular bombardment, at an internal pressure of 0.00068 m.m., or 0.9 M.

A shadow of an object inside a bulb can also be projected on to the opposite wall of the bulb by means of an outside pole. A mica cross is supported in the middle of the bulb (Fig. 20), and on connecting a small silvered patch, A, on one side of the bulb with the negative pole of the induction coil, and putting the positive pole to another patch of silver, B, at the top, the opposite side of the bulb glows with a phosphorescent light, on which the black shadow of the cross seems sharply cut out. Here the internal pressure is 0.00068 m.m., or 0.9 M.

Passing to the next phenomenon, I proceed to show the production of mechanical energy in a tube without internal poles. It is shown in Fig. 21 (P. = 0.001 m.m., or 1.3 M.). It contains a light wheel of aluminium, carrying vanes of transparent mica, the poles, A, B, being in such a position outside that the molecular focus falls upon the vanes on one side only. The bulb is placed in the lantern, and the image is projected on the screen; if I now pass the current you see the wheel rotates rapidly, reversing in direction as I reverse the current.

Here is an apparatus, Fig. 22, which shows that the residual gaseous molecules when brought to a focus produce heat. It consists of a glass tube with a bulb blown at one end and a small bundle of carbon wool, C, fixed in the centre, and exhausted to pressure of 0.000076 m.m., or 0.1 M. The negative electrode, A, is formed by coating part of the outside of the bulb with silver, and it is in such a position that the focus of rays falls upon the carbon wool. The positive electrode, B, is an outer coating at the other end of the tube. I pass the current, and those who are close may see the bright sparks of carbon raised to incandescence by the impact of the molecular stream.

You thus have seen that all the old "radiant matter" effects can be produced in tubes containing no metallic electrodes or volatilise. It may be suggested that the sides of the tube in contact with the outside poles become electrodes in this case, and that particles of the glass itself may be torn off and projected across and so produce the effects. This is a strong argument, which fortunately can be tested by experiment. In the case of this tube (Fig. 23, P. = 0.00068 m.m., or 0.9 M.) the bulb is made of lead glass phosphorescing blue under molecular bombardment. Inside the bulb, completely covering the part that would form the negative pole, A, I have painted a substantial coat of yttria, so as to interpose a layer of this earth between the glass and the inside of the tube. The negative and positive poles are silver disks on the outside of the bulb, A being the negative and B the positive pole. If, therefore, particles are torn off and projected across the tube to cause phosphorescence, these particles will not be particles of glass but of yttria, and the spot of phosphorescent light, C, on the opposite side of the bulb will not be the dull blue of lead glass, but the golden yellow of yttria. You see there is no such indication; the glass phosphoresces with its usual blue glow, and there is no evidence that a single particle of yttria is striking it.

Witnessing these effects I think you will agree I am justified in adhering to my original theory that the phenomena are caused by the Radiant Matter of the residual gaseous molecules, and certainly not by the torn off particles of the negative electrode.

(To be continued).

A NEW METHOD FOR STANDARDISING THE SOLUTIONS USED IN ALKALIMETRY AND ACIDIMETRY.

By EDWARD HART and STUART CROASDALE.

SEVERAL substances have been proposed and used as materials for determining the strength of the standard acid and alkaline solutions used in volumetric saturation analysis, among them sodium carbonate, oxalic acid, and acid potassium oxalate. All of these substances have disadvantages, especially where a great degree of exactness is necessary. Sodium carbonate, which, following Mohr's recommendation, has been most commonly used, is, as found in commerce, seldom quite pure. This was long ago pointed out by Stas. It has the further disadvantage that it must be ignited gently and weighed quickly after cooling, as it takes up moisture from the air quite rapidly. Another disadvantage is that the solution when titrated against an acid must be boiled to drive off carbon dioxide before the titration can be finished. All these things require time. As the volumetric method is especially designed to save time, these disadvantages are serious ones. The difficulty of getting oxalic acid of proper purity, and of protecting it from loss of water of crystallisation, is so well known that it need not be considered further. The same thing holds true, to some extent at least, of acid potassium oxalate. Any crystalline salt is sure to be subjected to more or less suspicion from the impossibility of so preparing it that no water shall be included between the crystals, or that no hygroscopic moisture shall be left adhering to the crystals, or that some of the water of crystallisation may have been driven off by too sharp drying. We have therefore devised a method which avoids all these sources of error, and which for exactness leaves nothing to be desired, and is extremely convenient and easy of execution.

The electrolytic assay of copper has long been known to yield very accurate results when properly carried out, but has recently been subjected to some criticism by English chemists. In order to test the matter, a very large number of analyses have been made in this laboratory, which will soon be ready for publication. The result of this investigation has convinced us that with proper precautions the assay is one of the most accurate known. In ordinary cases, where from 0.1 to 0.2 gm. copper are to be thrown down, the differences in duplicate assays never exceed 0.0002 gm., and generally do not exceed 0.0001 gm.

When normal copper sulphate is subjected to electrolysis, for every 63 parts copper thrown down 98 parts sulphuric acid are set free; and, if we use pure copper sulphate, at the end of the operation we shall have all the copper adhering to the dish, and a corresponding amount of pure sulphuric acid in solution. The copper is weighed as accurately as possible, and a simple calculation shows at once the amount of sulphuric acid in solution, which has thus virtually been weighed, and may be at once used for standardising caustic soda or other alkaline solution with which in turn standard acids can be compared.

A solution of pure copper sulphate when as dilute as this is not a very good conductor, and it is best, therefore, to add a small quantity of neutral potassium or sodium sulphate solution before the electrolysis is started.

The following examples illustrate the method, and show what accuracy can be attained when working in the ordinary rapid way.

Two roughly weighed samples of commercial C. P. copper sulphate were electrolysed, and gave—



- (1) 0.1015 = 0.15789
- (2) 0.1079 = 0.16784

$$0.2094 = 0.32573$$

Bleaching Wool and Silk with Hydrosulphite.—Gaston Dommergue.—This method is pronounced preferable to others on account of its simplicity and the low price of the materials.—*Moniteur Scientifique*, iv., Part 2.

The acid resulting was then used to standardise a caustic soda solution, which it was intended to dilute to decinormal strength. Phenolphthalein was used as indicator.

(1) required 3.4 c.c. of the caustic soda solution.

(2) " 3.6 " " " "

7.0

4.900

— = 15.043; 15.043 × 7 = 105.30

0.32573

In the above calculation, the atomic weight used for copper was 63, and the molecular weight of sulphuric acid was taken as 98. The decinormal solution was then made up, using 105.3 c.c. per litre of the strong solution.

A more careful calculation, using the atomic weight 63.18 for copper, and the molecular weight 97.82 for sulphuric acid, showed that the amount used was too small.

(1) 0.1015 Cu = 0.15715 H₂SO₄ = 3.4 c.c.

(2) 0.1079 " = 0.16706 " = 3.6 "

4.891

— × 3.4 = 105.808

0.15715

4.891

— × 3.6 = 105.39

0.16706

2) 211.198

105.599

The decinormal solution will therefore turn out to be too weak. This decinormal solution was then titrated against sulphuric acid obtained in the same way, as follows—

Decinorma soda, c.c.

(3) 0.1062 Cu = 0.16442 H₂SO₄ = 34.15

(4) 0.1065 " = 0.16495 " = 34.35

(5) 0.1049 " = 0.16241 " = 33.9

(6) 0.1060 " = 0.16412 " = 34.2

∴ c.c. will therefore equal $\left\{ \begin{array}{l} (3) 0.004814 \text{ H}_2\text{SO}_4 \\ (4) 0.004802 \text{ " } \\ (5) 0.004791 \text{ " } \\ (6) 0.004799 \text{ " } \end{array} \right\}$ Mean, 0.0048015

The behaviour of the solution at the point, when neutralisation was nearly reached, led us to suspect that the copper sulphate was not quite pure, for the solution became light pink, and this colour slowly faded. If another drop was added the same process was repeated, and this continued until four or five drops had been added, when the solution took a permanent pink tint.

We therefore prepared a new lot of copper sulphate by heating electrolytic copper with pure concentrated sulphuric acid, and re-crystallising the product eight times. Three determinations with this product gave the following results:—

(7) 0.1021 Cu = 0.1581 H₂SO₄ = 32.8 decinormal soda.

(8) 0.1041 " = 0.1612 " = 33.5 " "

(9) 0.1050 " = 0.1626 " = 34.1 " "

1 c.c. will therefore equal $\left\{ \begin{array}{l} (7) 0.0048194 \text{ H}_2\text{SO}_4 \\ (8) 0.0048112 \text{ " } \\ (9) 0.0047674 \text{ " } \end{array} \right\}$ Mean = 0.0047993.

Mean of 7 determinations, 0.0048006.

In (7) (8) and (9) the same fading of the pink tint occurred as in the first lot. This was traced to a little carbonate in the caustic soda, for when the solution, which had lost colour, was boiled, the pink tint reappeared. We have no doubt that with a burette with

very fine point, still closer results can be obtained; but for any ordinary work the above are sufficiently accurate. — *Journal of Analytical Chemistry*, Vol. iv., Part 4.

NOTICES OF BOOKS.

Elementary Systematic Chemistry. For the Use of Schools and Colleges. By W. RAMSAY, Ph.D., F.R.S., Professor of Chemistry in University College, London. London: J. and A. Churchill.

THIS manual is in several respects superior to the bulk of its rivals in this very crowded field of literature. It is not arranged "to meet the requirements" of any particular examination. It is not fitted up with an appendix of questions which have been put on any occasions, and which possibly may recur. Above all, its teachings are really systematic. Those elements and compounds are described which may serve as types of classes. The information given, e.g., the atomic weights, is correct according to the most recent determinations. The insertion, at the beginning of the work, of a few brief chapters on chemical physics, is a return to a useful custom which has been too generally abandoned.

The remark, in "Lesson I.," that we do not know matter apart from energy, is suggestive. Did it occur, should we recognise it as matter?

The date assigned to the discovery of the periodic arrangement of the elements by Newlands is here given as 1866-68. This is surely a slip of the pen, as the earliest communications of Mr. Newlands appeared in the *CHEMICAL NEWS* in 1863-64. The author, very justly, does not accept the classification of the elements as metals and non-metals.

The index is exceedingly complete, and the work is one that we can recommend in preference to at least three-fourths of the existing elementary manuals of chemistry.

Recovery of Hydrochloric Acid from Waste Products. (Turner's Patent). London: W. J. Fraser and Co.

THE waste products here referred to seem to be the spent "pickle" used in certain departments of the iron trades. At the same time, the process here described would be applicable to other liquid wastes. The refuse in question is considerable in quantity, and has already tasked the ingenuity of chemists. It can no longer, as of old, be simply run into the nearest stream. Its neutralisation with limestone is unremunerative, whilst the motive for its recovery is strengthened by the certainty that the price of hydrochloric acid must ultimately rise.

The Turner process is exceedingly simple and inexpensive, and appears to be quite successful. The waste pickle, an impure solution of ferrous chloride along with a certain quantity of free acid, is run continuously into a furnace of peculiar construction. Here it is decomposed, as we learn, into hydrochloric acid and ferric oxide. The latter product is raked out of the furnace as it accumulates, and is used for "fettling" in the puddling process. The acid is condensed in a series of cooling pipes and serves over again in the galvanising process, being of the same strength as that originally used for pickling. The economical features of the process are most satisfactory; only 4 cwts. of fuel are used for every ton of the waste liquor treated. The plant is not costly, and, as it works at a low temperature, the wear and tear are small. No skilled labour is employed, one labourer being sufficient to attend to a plant of the largest size. According to the actual experience of a firm who have worked the process since July, 1889, the recovery of one ton of acid of a quality fit for use in pickling costs eight shillings.

Few processes for utilising waste products can show such good results.

Biographisch-literarisches Handwörterbuch der Wissenschaftlich bedeutenden Chemiker. ("Biographical-Literary Dictionary of Chemists who are Scientifically of Importance.") Herausgegeben von Dr. CARL SCHÄEDLER. Berlin: R. Friedlaender and Sohn.

It sometimes happens that we feel uncertain as to the time and place when some chemist "flourished," as to his researches and discoveries, the works he wrote, or the positions he filled. Dr. Schaedler's compact little work meets this want in a very convenient manner. The notices of the various chemists here mentioned are necessarily brief, but they are almost without exception accurate. The work is characterised of a spirit of fairness and impartiality. There is no tendency to unduly exalt German *savants* at the cost of their French or English contemporaries. A similar impartiality is observed as between the different tendencies which spring up within the field of chemical science. We notice with pleasure that the author pronounces Baumé's hydrometer "erratical." Chemists who read German will find this work exceedingly useful.

CORRESPONDENCE.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—*Post hoc ergo propter hoc* is but a *prima facie* argument, and surely not one upon which agitators may be allowed to claim that they have brought about a so-called reform.—I am, &c.,

NEMO.

THE JUBILEE OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—I venture to suggest that the Jubilee of the Chemical Society be in part celebrated by the foundation of a Benevolent Fund for the relief of distressed Fellows and others, and of their widows and orphans; to be administered by the Society, alone or in conjunction with the Institute of Chemistry and the Society of Chemical Industry.

I will gladly give £50 if nineteen other subscribers will each contribute a like sum. The few wealthy chemists amongst us would probably promise much larger amounts.

The Fund once started, doubtless many chemists would contribute a guinea annually.—I am, &c.,

JOHN ATTFIELD.

Watford, Feb. 17, 1891.

STARCH-PAPER TEST FOR IODINE.

To the Editor of the Chemical News.

SIR,—While analysing qualitatively a mixture containing iodides and bromides the other day, it occurred to me, as my starched paper (prepared according to the careful directions of the text-books) was done, and I was disinclined to break off my work to make more, that I might find an efficient substitute in ordinary white writing-paper. I tried this after moistening with water, and found to my delight that it did as well as the best starch-paper that ever was prepared; and why not, seeing that in the process of manufacture, writing or, indeed, any common paper is finished with size which contains a notable quantity of starch?

As I had never before heard of this simple and ready substitute, I thought the notice of it might be welcome to

other analysts, to whom, like everyone else worthy of existence, time is money.—I am, &c.,

ALEX. JOHNSTONE.

Mineralogical Laboratory
University of Edinburgh.
Feb. 14, 1891.

AMERICAN COPYRIGHT.

To the Editor of the Chemical News.

SIR,—In view of the several favourable criticisms of my "Manual of Assaying," which have appeared in the *CHEM. NEWS* from time to time, I trust you will insert this protest against the "reprint" noticed in the issue for Dec. 5, 1890. This "copy" is issued entirely without the authority of my publishers or myself, and could not possibly have been put forward had there been any International Copyright Law. The fact that many American publishers have "pirated" English publications could hardly be tendered as an apology for this re-issue. The reprint is backed as "Brown and Griffiths." The actual contribution of Prof. Griffiths is one chapter on "Fuels," and, presumably, the slight revision, consisting of the elimination of the personal "I" in favour of the editorial "we," and the substitution of English financial values for American ones.

While we may not expect the utmost ideas of honour from publishers, certainly we do expect the highest order of action from scientists; and it was therefore with feelings the most mingled, of surprise, sorrow, and indignation, that I saw the name of so distinguished a man as Prof. Griffiths attached to the book I protest against.—I am, &c.,

W. LEE BROWN.

Author of Brown's "Manual of Assaying."

Office of North-western Gas-Light
and Coke Co., Evanston, Ill.
Jan. 27, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxii., January 26, 1891.

Contributions to the History of the Nitrogenous Principles Contained in Vegetable Soils.—M. Berthelot and G. André.—The author studies the action of acid and alkaline solvents upon the organic nitrogen (previously insoluble) contained in vegetable soils. By the prolonged action of alkalis we may render soluble, in 26 hours' treatment in the water-bath, 93.6 per cent of the organic nitrogen of soils. By the successive action of alkalis and acids we may extract 95.5 per cent. If we begin with dilute hydrochloric acid, 71 per cent of the nitrogen are rendered soluble by 13 hours' treatment in the water-bath, and the subsequent action of dilute potassa brings the total thus made soluble up to 91 per cent. These experiments show how the insoluble nitrogen contained in the humic compounds is gradually rendered soluble and capable of assimilation. The action of plants is certainly not comparable to that of the alkalis and acids used in the author's experiments; but the natural agents compensate for their smaller energy by their prolonged action.

New Observations on the Volatile Nitrogenous Compounds given off by Vegetable Mould.—M. Berthelot.—The exhalation of nitrogenous products proceeds as long as the earth is humid. If it is dry the phenomenon in question is beyond comparison slower, though it still

goes on. The nitrogen contained in the volatile organic compounds given off by sandy clays is always much greater in quantity than that escaping as ammonia. From a true vegetable soil the quantities are equal.

Experiment on the Synthesis of Proteic Compounds.—P. Schutzenberger.—This memoir will be inserted in full.

On the Application of the Measure of the Rotatory Power to the Determination of the Compounds Formed by Aqueous Solutions of Malic Acid with the White Alkaline Phosphomolybdates.—D. Gernez.—This memoir is not adapted for useful abstraction.

The Conductivity of Isomeric Organic Acids and of their Salts.—Prof. Ostwald.—The author contests the novelty or originality of the results signalled in a communication by D. Berthelot (*Comptes Rendus*, January 5th, 1891, p. 46).

Reply to Professor Ostwald.—D. Berthelot.—The author contests the reclamation of Prof. Ostwald.

The Mordants, used in Dyeing and the Theory of Mendeleeff.—M. Prud'homme.—This memoir will be inserted in full.

Note on Diabetes.—H. Arnaud.—This paper is more physiological than chemical in its character.

Revue Générale des Sciences Pures et Appliquées.
Vol. ii., No. 1, January 15, 1891.

The Artificial Reproduction of the Ruby.—A. Verneuil.—M. Frémy, in conjunction with the author, has improved his process. He has obtained not only the ruby but the sapphire, and even the oriental emerald, by modifying the quantity of chrome employed. The most suitable temperature for the reaction appears to be about 1350°. The largest stones obtained weigh a little more than 75 m.grms., or one-third of a carat; but he hopes, by working on a larger scale, to produce specimens of one or two carats.

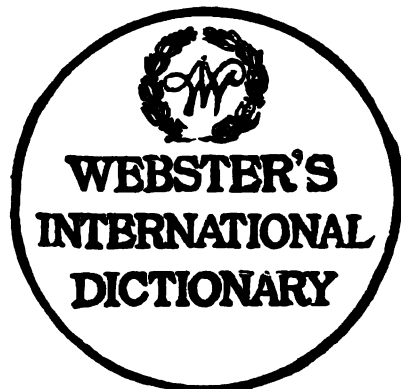
Revue Universelle des Mines et de la Metallurgie.
Vol. xii., No. 2.

This issue contains no chemical matter.

MEETINGS FOR THE WEEK.

- MONDAY, 23rd.**—Medical, 8.30.
— Society of Arts, 8. "The Electric Transmission of Power," by Gisbert Kapp.
- TUESDAY, 24th.**—Institute of Civil Engineers, 8.
— Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley, F.R.S.
— Royal Medical and Chirurgical, 8.30.
- WEDNESDAY, 25th.**—Society of Arts, 8. "Colonisation and its Limitations," by E. J. Ravenstein.
— Geological, 8.
— Royal, 4.30.
- THURSDAY, 26th.**—Institute of Electrical Engineers, 8.
— Royal Institution, 3. "The Position of Lull, Purcell, and Scarlatti in the History of the Opera," by Professor C. Hubert H. Parry.
— Society of Arts, 4.30. "The Economic Development of Siam," by Robert Gordon.
- FRIDAY, 27th.**—Royal Institution, 9. "The Art of Acting," by Percy Fitzgerald.
— Society of Arts, 4.30. "The Science of Colour," by Captain Abney.
— Physical, 5. (1) "Proof of the Generality of Certain Formulæ Published for a Special Case by Mr. Blakeley; Tests of a Transformer," by Prof. W. E. Ayrton and Mr. J. F. Taylor. (2) "Further Contributions to Dynamometry," by Mr. T. H. Blakeley. (3) Note on Electrostatic Wattmeters," by Mr. Swinburne. (4) "Interference with Alternating Currents," by Prof. W. E. Ayrton and Mr. Sumner.
- SATURDAY, 21th.**—Royal Institution, 3. "The Forces of Cohesion," by The Right Hon. Lord Rayleigh.

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PATENTS, DESIGNS, & TRADE MARKS ACTS
1883 TO 1888.

NOTICE IS HEREBY GIVEN that HORACE KORCHLIN, of Loerrach, in the German Empire, has applied for leave to amend the Specification of the Letters Patent No. 4899 of 1881 granted to John Murray for "Improvements in the manufacture of Colouring Matters."

Particulars of the proposed Amendment were set forth in the Illustrated Official Journal (Patents), issued on the 11th February, 1891. Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C. of opposition to the Amendment within one calendar month from the date of the said Journal.

(Signed) **H. READER LACK,**
Comptroller-General.

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London Agents, **COSTE and Co.**, 19 and 20, Water Lane, Tower Street, E.C., who hold stock ready for delivery.

THE CHEMICAL NEWS.

VOL. LXIII., No. 1631.

PHOTO-CHEMICAL RESEARCHES.*

By Professor V. SCHUMANN.

I HAVE unfortunately not been able to continue my spectroscopic photographs on account of the severe weather; but I have been able to carry on the photo-chemical part of my investigations, and not without some results. I have studied the absorption spectrum of AgBr at higher temperatures, and have found that melted AgBr has a very dense absorption band near "D," and if heated still more strongly it absorbs almost all the rays of the visible spectrum. In presence of AgI all the maxima of AgBr are displaced towards the red. This displacement is not the same in all maxima, but increases with their wave-length. This refers also to the maximum of illumination, which appears at the wave-length 630. The circumstance that the dark rays effect the absorption of the luminous rays, whereby probably the photographic sensitiveness is increased, will help me to photograph the infra-red. I purpose observing this region with the aid of my fluorite train. I expect a good result from the use of fluor-spar, because it possesses a distinguished diathermance as regards refraction and dispersion, and is therefore less affected by heat than any other optical medium. I renounce rock-salt because its transparency, as its refractive planes become dim, is not sufficiently constant, and does not suffice for permanent insolation, whatever its diathermance may be when freshly polished.

AgBr displays very peculiar structures. I have latterly been able to obtain it in the shape of the fig cactus (*Opuntia*), certainly only in a tender microscopic form. I can distinguish these structures only with apochromatic object-glasses, and with the rays of the illuminating lens falling at right angles to the objective axis. All my apochromatic lenses have been obtained from the workshops of Carl Zeiss, of Jena.

H. W. Vogel, in opposition to Abney, maintains that there exist two modifications of AgBr photographically distinct. One of them, if previously dried and if it had been precipitated in alcohol, can not be suspended in gelatin. The other, it is alleged, which has been precipitated from watery solutions, can, on the contrary, not be diffused in collodion. Extended experiments have convinced me that no such difference exists. It may easily happen that the phenomenon observed by Herr Vogel is manifested, especially if too high a temperature has been used in drying the precipitate. AgBr always becomes incapable of suspension if dried in hot air. This is the case whether it has been precipitated from alcohol or from water. If one precipitate has been treated at a much higher temperature than another, the phenomenon reported by Herr Vogel may easily have been manifested.

This, in fact, happened to me in the outset of my experiments on this subject; but on going to work more cautiously, and drying both precipitates quite equally, at the respective temperatures of 15°, 80° and 160°, I arrived at opposite results.

At 15° the aqueous and the alcoholic AgBr were found capable of suspension in collodion and in gelatin. At 60° the capability of suspension of both is much reduced, and at 160° I attempted in vain to emulsify AgBr. I cannot, therefore, admit the statements of Vogel, the less as, on the other hand, his allegation that gelatin is only a feeble sensitiser in my recent series of experiments,

encounters still stronger contradictions. I shall at an early date demonstrate that gelatin is absolutely a powerful sensitiser.

I have likewise been unable to detect a spectral difference of the two precipitates when they are suspended in gelatin. In all proofs there appeared the same spectrum which the ordinary silver-bromide gelatins display. The slight displacements which occur in my spectrograms are solely due to atmospheric fluctuations. I have not yet succeeded in a simultaneous and contiguous illumination of both emulsions, and it might hence be inferred that the photographic action of the sunlight in my proofs had varied exceptionally, and thus occasioned the difference from the observations of Herr Vogel. But however justifiable such an argument might seem, its validity is at once enfeebled by the circumstance that the spectral proofs from both emulsions were taken in rapid succession. Hence so considerable a displacement as Vogel calls is exceedingly improbable. On the other hand, it is not conceivable that my instrument can have occasioned the discrepancy. I have in these operations used only the most accurate and sensitive spectrographic apparatus which my cabinet includes.

A SIMPLE ELECTRICAL SAW.

By H. N. WARREN, Research Analyst.

WHENEVER a powerful electrical circuit is closed by a platinum wire of suitable dimensions, the well-known heating effect of the same is at once manifested; yet no one seems to have been struck with the idea that the simple heated wire may be employed as a most effective disintegrator of the hardest organic compounds. A similar but more convenient article may be constructed as follows. It consists of two upright pieces of very stout brass or copper wire, connected at the lower extremities by a non-conducting medium, while across the top is secured a piece of moderately thin platinum wire. On thus connecting the apparatus by means of side binding screws to the terminals of about four Bunsen batteries, the platinum wire at once becomes heated to bright redness, and will be found to cleave the hardest wood with great facility, inasmuch that a large number of useful appliances may be thus manufactured in a short space of time. Owing, however, to the platinum wire frequently breaking, probably on account of its intimate contact with the carbon, whilst at an elevated temperature, the author has devised and used with advantage a modified wire, formed by depositing metallic platinum upon fine steel wire, by exposing that substance to the action of a slow electrical current, in contact with an ethereal solution of platinum chloride.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

Appointment.—The Professor of Agriculture at the Royal Agricultural College, Cirencester, Professor James Muir, M.R.A.C., F.C.S., has been promoted to the newly endowed Chair of Agriculture at the Yorkshire College, Leeds. Mr. Muir has had a distinguished career both as student and lecturer, and the Leeds College is to be congratulated at having secured his services.

International Congress of Geologists.—We learn that the 5th meeting of the Congress will be held at Washington, on August 26th next. Persons wishing to be present are requested to announce their intention to the Secretary's Office, 1330 F. St., Washington, D.C. The fee is 2½ dollars. Special reduced rates will be charged by the steamship lines from Europe, and by the railway companies on occasion of the geological excursions.

* Extracts from a letter to the Editor.

ELECTRICITY
IN TRANSITU:
FROM PLENUM TO VACUUM.*

By WILLIAM CROOKES, F.R.S.,
President of the Institution of Electrical Engineers.

(Continued from p. 93).

Phosphorescence in High Vacua.

I HAVE already pointed out that the molecular motions rendered visible in a vacuum tube are not the motions of molecules under ordinary condition, but are compounded of these ordinary or kinetic motions and the extra motion due to the electrical impetus.

Experiments show that in such tubes a few molecules may traverse more than a hundred times the *mean* free path, with a correspondingly increased velocity, until they are arrested by collisions. Indeed, the molecular free path may vary in one and the same tube, and at one and the same degree of exhaustion.

Very many bodies, such as ruby, diamond, emerald, alumina, yttria, samaria, and a large class of earthy oxides and sulphides, phosphoresce in vacuum tubes when placed in the path of the stream of electrified molecules proceeding from the negative pole. The composition of the

numerous experiments I find that bodies will phosphoresce in actual contact with the negative pole.

This is only a temporary phenomenon, and ceases entirely when the exhaustion is pushed to a very high point. The experiment is one scarcely possible to exhibit to an audience, so I must content myself with describing it. A U-tube, shown in Fig. 25, has a flat aluminium pole, in the form of a disk, at each end, both coated with a paint of phosphorescent yttria. As the rarefaction approaches about 0.5 m.m. the surface of the negative pole A becomes faintly phosphorescent. On continuing the exhaustion this luminosity rapidly diminishes, not only in intensity, but in extent, contracting more and more from the edge of the disk, until ultimately it is visible only as a bright spot in the centre. This fact does not prop a recent theory, that as the exhaustion gets higher the discharge leaves the centre of the pole, and takes place only between the edge and the walls of the tube.

If the exhaustion is further pushed, then at the point where the surface of the negative pole ceases to be luminous, the material on the positive pole, B, commences to phosphoresce, increasing in intensity until the tube refuses to conduct, its greatest brilliancy being just short of this degree of exhaustion. The probable explanation is that the vagrant molecules I introduce in the next experiment, happening to come within the sphere of influence

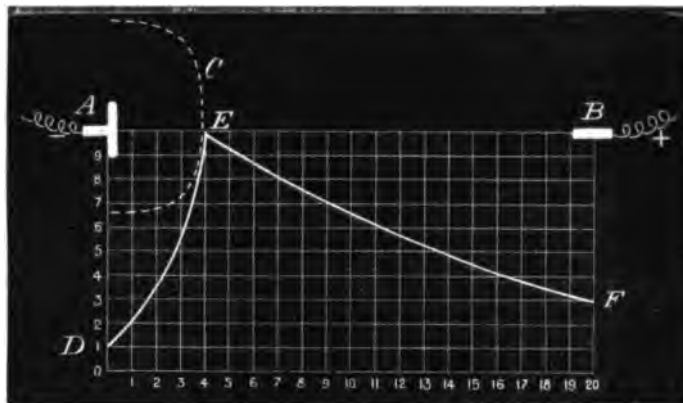


FIG. 24.—P. = 0.25 m.m., or 330 M.

gaseous residue present does not affect phosphorescence; thus, the earth yttria phosphoresces well in the residual vacua of atmospheric air, of oxygen, nitrogen, carbonic anhydride, hydrogen, iodine, sulphur, and mercury.

With yttria in a vacuum tube the point of maximum phosphorescence, as I have already pointed out, lies on the margin of the dark space. The diagram (Fig. 24) shows approximately the degree of phosphorescence in different parts of a tube at an internal pressure of 0.25 m.m., or 330 M. On the top you see the positive and negative poles, A and B, the latter having the outline of the dark space shown by a dotted line, C. The curve D, E, F, shows the relative intensities of the phosphorescence at different distances from the negative pole, and the position inside the dark space at which phosphorescence does not occur. The height of the curve represents the degree of phosphorescence. The most decisive effects of phosphorescence are reached by making the tube so large that the walls are outside the dark space, whilst the material submitted to experiment is placed just at the edge of the dark space.

Hitherto I have spoken only of phosphorescence of substances placed under the negative pole. But from

of the positive pole, rush violently to it and excite phosphorescence in the yttria, whilst losing their negative charge.

Loose and Erratic Molecules.

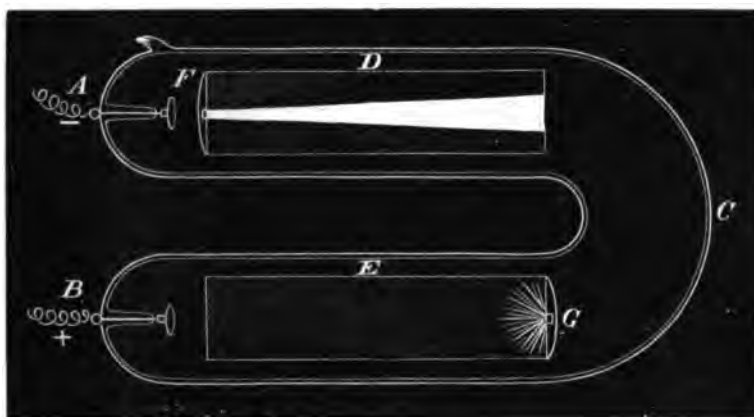
In the brief time left to me this evening I cannot touch upon the mass of experiments made to render this result clear, so I will at once show you a piece of apparatus that clearly illustrates the cause of phosphorescence at the positive pole. A drawing of this tube is shown at Fig. 26, but let me first explain the effect I expect to obtain, and then endeavour to show the actual experiment.

A C B is a U-shaped tube with terminals, A and B, at each end; D and E are two mica screens covered with a phosphorescent powder, having at F and G other screens with a small slit in front, so as to allow only a narrow beam of charged molecules to pass through. At first the tube is exhausted to a pressure of 0.006 m.m., or 100 M., and you see how sharp and slightly divergent is the luminous image on screen D, whilst not a trace of phosphorescence is to be seen on the screen E in the other limb of the tube. Now I push the exhaustion to the highest point short of non-conduction (0.000076 m.m. or 0.1 M.), and the phenomena change. The initial line of light on D becomes wider and unsteady, whilst at the gate, G, a decided phosphorescence is observable entering the second

* Inaugural Address delivered January 15th, 1891.



FIG. 25.



P. = 0.076 m.m.,
or 100 M.

P. = 0.000076 m.m.,
or 0.1 M.

FIG. 26.

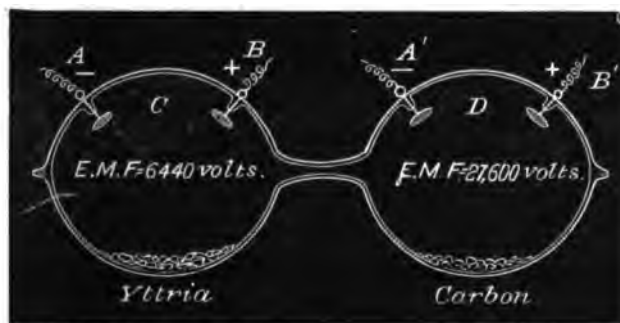


FIG. 27.—P. = 0.02 m.m., or 26 M.

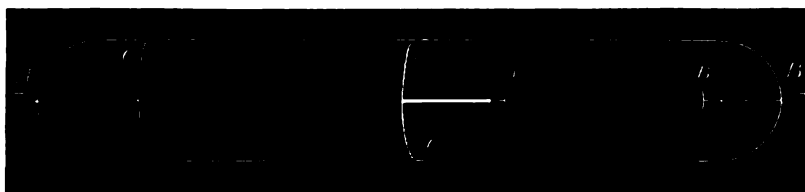


FIG. 28.—P. = 0.00068 m.m., or 0.9 M.

screen, &c. This luminosity diverges to a considerable extent, much more than did the stream of charged molecules observed in the first limb of the tube at the lower exhaustion. This is only to be expected, inasmuch as those sparse molecules which have run the gauntlet of the crowd and have been hunted and buffeted round the corner will have little or no lateral support, but wander to the furthest end of the tube, and altogether behave differently to the orderly procession of molecules at more moderate exhaustion.

The Resistance of High Vacuum.

I must only lightly touch this phenomenon to-night; it is a subject of deep interest, and one to which I have lately devoted much time. Shortly I hope to publish a full account of results recently obtained.

The passage of an induction current at a high vacuum through a tube depends much upon the material of the tube or the substance enclosed within it. Given the same degree of exhaustion, and the same distance between the terminals inside the tube, the E.M.F. necessary to force the current through may vary from 3000 volts to 20,000 volts, according to the particular material used.

Here is a very striking example that will serve to illustrate this phenomenon. Fig. 27 is a double tube joined by a narrow open channel and therefore in the same state of exhaustion throughout (P. = 0.02 m.m., or 26 M.). Each tube is furnished with a pair of poles, A, B, and A', B'. One tube contains the phosphorescent earth yttria, the other contains finely divided carbon. I first connect the yttria tube, C, to the coil, and place in parallel circuit with it a spark gauge. To begin with, this gauge is set to a gap of 1 m.m. (An E.M.F. of 920 volts is necessary to strike across 1 m.m. of air; therefore the difference of potential at the terminals inside the yttria tube is 920 volts, and this you perceive is not sufficient to force the current through the tube). I now gradually open the gauge until the potential of the inner terminals has risen to a point high enough to allow the spark to pass through the tube, making the yttria phosphorescent.

The gap is at 7 m.m. equal to an E.M.F. of 6440 volts. I next attach the coil wires to the tube D containing the carbon, and the exhaustion in the tubes being the same as before, I repeat the experiment; you now see that the gap has to be opened to 30 m.m., equivalent to an E.M.F. of 27,600 volts, before the current will pass through the tube. The fact of whether the vacuum tube contains yttria or carbon makes a difference of 21,160 volts in the E.M.F. required to cause a discharge between the terminals.

One other experiment I would like to show in further illustration of this resistance. The idea suggested itself that possibly differences in the material or conductivity of the particular bulbs might influence the results you have just seen. Here (Fig. 28) is a long cylindrical tube of phosphorescent Bohemian glass containing a pair of terminals, A, B; it also contains a shorter cylinder of glass, C, C, brightly silvered inside. The internal pressure is 0.00068 m.m., or 0.9 M. The silver cylinder is now at one end of the tube out of the way of the terminals, which therefore have phosphorescent glass around them. I turn on the coil and find that the E.M.F. necessary to force the current through, now that the terminals are in a phosphorescent chamber, is 1380 volts. I slide the cylinder down to the end of the tube so as to inclose the terminals in a metallic silver chamber, and you see the E.M.F. necessary to pass the current rises to 6440 volts. Metallic silver does not phosphoresce, whilst Bohemian glass phosphoresces very well. It appears that the greater the phosphorescing power of the substance surrounding the poles so much the easier does the induction spark pass. Surround the poles with Bohemian glass or yttria—two phosphorescent non-conductors of electricity—and the induction spark passes easily; immediately I surround the terminals with a non-phosphorescent conductor the current refuses to pass.

(To be continued).

DETERMINATION OF WATER IN SUPERPHOSPHATES.

By JULIUS STOKLASA.

The author's extensive experiments both with chemically pure monophosphates and with such as are mixed with free phosphoric acid show to what transformations the hygroscopic water and that in chemical combination are exposed. An accurate study of all the chemical processes taking place with the joint action of sulphates and tri- and di-phosphates is required to lead to an accurate method of determination.

1. Influence of Temperature upon Monocalcium Phosphate.

As the experiments of Birnbaum upon the influence of temperature upon monocalcium phosphate are in some degree unexplained and incomplete, the author resolved to repeat them. The experiments were carried out with the chemically pure preparation of the following composition:—

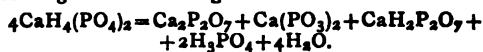
CaO	..	..	..	..	22.36	per cent.
P ₂ O ₅	..	..	..	..	56.67	"
H ₂ O	..	..	..	..	21.53	"

containing 0.014 per cent of free phosphoric acid. In the first place, 3.59 grms. of the compound were dried at 100°.

The loss of water in 10 hours was	1.83
"	20
"	30
"	40
"	50

This loss of water, 6.43 per cent, remained constant, for no further decrease of weight was observed below 100°. This quantity of water corresponds to 1 molecule. $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ therefore loses its crystalline water at 100°, but only in 50 hours. The calcium phosphate thus obtained forms opaque crystals, not hygroscopic, which were found to contain 24.02 per cent CaO, 60.74 P₂O₅, and 15.00 per cent H₂O.

It dissolves in water very slowly and without decomposition in the proportion 1:200. The temperature in drying may reach 105° without any perceptible change in the monocalcium phosphate. But if dried at 105° for longer than 20 hours it undergoes a further decomposition, though to a slight extent. The decomposition is promoted if the temperature is gradually raised to 200°, according to the following scheme:—



If water acts upon such dried calcium phosphate (in the proportion 1:200) the undecomposed monocalcium phosphate by the monocalcium pyrophosphate and the phosphoric acid dissolve, whilst the pyro- and meta-calcium phosphate remain undissolved.

The experiment in question was carried out as follows:—The monocalcium phosphate was dried in a platinum capsule at 105°—200°, and in a very thin layer, so that the temperature might be uniform. The loss of water was determined at fixed intervals, and the dried monocalcium phosphate was afterwards dissolved in water at 15° in the proportion of 1:200. In the filtrate the free phosphoric acid and the total orthophosphoric acid were determined in part directly by means of uranium acetate, and in part with molybdic mixture after the solution had been boiled with nitric acid. Lastly, the calcium oxide was determined. The part insoluble in water was collected on the filter, and in it the phosphoric acid and the calcium oxide were determined.

5.0 grms. monocalcium phosphate were dried for an hour at 200°. The loss of water was 7.20 per cent. Therefore, according to the equation given above, 50.4 per cent of monocalcium phosphate had been decomposed. The dried substance was mixed with a litre of water. The

undissolved residue of pyro- and meta-phosphate, after being shaken for an hour, was filtered through a weighed filter, washed, dried at 120°, and weighed. The dried substance was dissolved in *aqua regia*, the excess of acid evaporated off, and the solution diluted to $\frac{1}{2}$ litre.

The analysis showed:—

CaO	36.81 per cent.
P ₂ O ₅	62.20 "

or by calculation:—

CaO	37.12 per cent.
P ₂ O ₅	62.88 "

The analysis showed 23.15 per cent pyro- and meta-calcium phosphate (by calculation 22.42 per cent), and these have been separated out:—

Ca ₂ P ₂ O ₇	12.6 per cent.
Ca(PO ₃) ₂	9.82 "

In all experiments the author found in the amorphous matter thus separated out 62–63 per cent P₂O₅, and 36–37 per cent CaO if the original monocalcium phosphate had been dried at 110–190°.

During drying there is separated out neither pure pyrophosphate, as Birnbaum conjectured, nor meta-phosphate, as Joulie and Millot maintain.

In the aqueous solution of the dried monocalcium phosphate there was first determined the free phosphoric acid by titration with decinormal potassa, with methyl orange as indicator. There was found 6.66 per cent P₂O₅, corresponding to 9.2 H₃PO₄, or by calculation, 9.72 per cent H₃PO₄.

If the total orthophosphoric acid in the solution is determined by titration by means of uranium acetate, the results will always be lower than when the molybdenum method is used. The difference is occasioned by the phosphoric acid which is contained in the solution as monocalcium pyro-phosphate. This compound may be converted into monocalcium orthophosphate by boiling with a few drops of nitric acid.

Whilst the titration of the solution showed 35.8–36.0 per cent phosphoric acid after heating with nitric acid (0.55 gm. HNO₃ to 25 c.c. of solution and boiling for thirty minutes), there were found by the molybdenum method 42.70–42.90 per cent phosphoric acid.—*Zeitschrift Anal. Chemis.*

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 5th, 1891.

Dr. W. J. RUSSELL, F.R.S., in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Albert Edward Bell, Sherborne School, Sherborne, Dorset; Rhys Pendrill Charles, Plas Newydd, Neath; Gilbert John Fowler, Dalton Hall, Victoria Park, Manchester; Berington H. Gibbins, Ocala, Florida, U.S.A.; J. A. R. Greaves, Old Rectory, Grappenhall, Cheshire; William Beaumont Hart, Gransmoor Avenue, Fairfield, near Manchester; Rev. Edgar Norman Langham, M.A., St. John's College, Cambridge; James Leicester, 3, Queen's Parade, Brandon Hill, Bristol; William Macdonald, 109, Crofton Road, Peckham, S.E.; Frederick Johnson Merrils, 65, Roe Lane, Pitsmoor, Sheffield; George R. Morrison, Richmond House, Plaistow; Lewis Ough, 15, Upper King Street, Leicester; James Ashburner Storey, Moorside, Lancaster; Albert Searl, The Caxtons, Miskin Road, Dartford.

It was announced that the following changes in the Council list were proposed by the Council:—

As President, Professor Crum Brown, *vice* Dr. Russell. As Vice-Presidents, Mr. J. Pattinson and Professor Tilden, *vice* Professors Crum Brown and Mallet.

As Foreign Secretary, Professor Meldola, *vice* Professor Japp.

As Members of Council, Dr. Atkinson, Mr. Boverton Redwood, Professor Perkin, and Dr. J. Voelcker, *vice* Mr. Cross, Professor Dunstan, Professor Meldola, and Dr. Plimpton.

The following papers were read:—

5. "The Formation of an Explosive Substance from Ether." By Professor P. T. CLEVE.

The author, in the course of a letter to the Secretary, describes a remarkable explosion occasioned by impurities in commercial ether. On distilling about 250 c.c. of the ether, it was noticed that a viscid residue remained; after drying on the water-bath, this formed a transparent amorphous mass, estimated to weigh about 0.75 gm. Prof. Cleve states that, having poured a little water on to the substance, he proceeded to stir it gently with a rounded glass rod; this occasioned a most violent explosion. A number of the pieces of glass which were projected about perforated the windows just as if they had been revolver bullets. The explosive substance was probably ethyl peroxide, as it gave the well-known perchromic colouration, besides liberating iodine and discharging oxygen from silver oxide; it was at once destroyed by reducing agents; it exploded with as much violence as if it had been chloride of nitrogen or fulminate.

DISCUSSION.

Professor DUNSTAN remarked that several cases had been recorded of explosions during the distillation of impure ether, one a few years ago by Schaer in the *Archiv. der Pharmacie* for 1877.

6. "Does Magnesium form Compounds with Hydrocarbon Radicles?" By ORME MASSON, M.A., D.Sc., and U. T. M. WILSMORE, B.Sc., University of Melbourne.

According to Hallwachs and Schafarik (*Annalen*, cix., 206), magnesium in the form of filings and ethyl iodide commence to interact at ordinary temperatures, and the interaction is complete at 180°; they state that the metal becomes converted into a white mass, the liquid disappearing, much gas being generated. On heating the white mass, a colourless volatile liquid distilled over, which fumed strongly in the air, but did not inflame; this liquid, it was believed, consisted of hydrocarbons mixed with traces of magnesium ethide, but, as the residue decomposed water with explosive violence, it was thought that it contained a considerable amount of magnesium ethide combined with magnesium iodide.

Cahours (*Annales de Chimie et de Physique* [5], xviii., 17) also found that much heat was evolved on adding methyl or ethyl iodide to magnesium filings. Having digested a mixture of the metal and ethyl iodide at 130° till the liquid had disappeared, he heated the resulting white mass in an atmosphere of hydrogen, and obtained a liquid distillate which took fire in the air and acted strongly on water. Carbon and hydrogen were estimated in two fractions of this liquid, but the results were far from agreeing with the theoretical values; the discrepancies were attributed to insufficient purification. No evidence of the presence of magnesium in the product was adduced by Cahours.

Wanklyn heated sodium zinc ethide with mercury and magnesium wire, and obtained a white, spontaneously inflammable, solid product. This contained magnesium and zinc, but only traces of sodium; it was believed to be magnesium zinc ethide.

The authors state that they have in vain endeavoured to prepare magnesium ethide (1) from magnesium and ethyl iodide; (2) from magnesium copper couples and ethyl iodide; (3) from an alloy of magnesium and sodium and ethyl iodide; (4) from magnesium and zinc ethide; (5) from magnesium and mercury ethide; and (6) from anhydrous magnesium iodide and zinc ethide.

An alloy formed by heating magnesium and sodium together in a hard glass flask in an atmosphere of hydrogen acted very slowly on ethyl iodide at 100°, and no signs of the formation of magnesium ethide were observed. On heating together magnesium and zinc or mercury ethide in sealed tubes, no action occurred till the temperature rose sufficiently high to decompose the ethide; large quantities of gas were then formed, zinc or mercury separating, but no magnesium ethide. Similarly, magnesium iodide and zinc ethide appeared not to interact, the ethide being decomposed simply by the heat.

There appeared to be little or no advantage in using magnesium copper couples, the action being in all respects similar to that of magnesium alone, although occasionally somewhat quicker. Magnesium iodide and gaseous hydrocarbons were the sole products.

Several experiments on the action of ethyl iodide on magnesium were tried under varied conditions and using the two substances in different proportions; sometimes a crystal of iodine was added as recommended by Frankland for the preparation of zinc chloride. In most cases the materials were heated together in a flask connected to a reflux condenser, from which the air was displaced at the outlet by hydrogen or carbon dioxide. The magnesium used was prepared by fusing commercial ribbon in an iron crucible under a flux of ammonium, magnesium, and potassium chlorides, and subsequently filing down the lump; it was practically free from impurities except traces of iron. The results obtained were uniformly negative, and although previous observers have stated that interaction occurs at ordinary temperatures, the authors have never perceived the slightest sign of action till after the iodide and metal had been heated together for some time. Thus, in an experiment in which 30 grms. of specially dried ethyl iodide was added to 5 grms. of magnesium, and the temperature of the bath containing the flask was maintained a little below 100°, no action seemed to take place for a time, but after a while gas was given off and a white powder was seen to slowly form on the metal; after thirty hours' continuous heating, ethyl iodide ceased to run back, and the evolution of gas—which had been continuous—came to an end. On heating the residue to 270°, no distillate except a little unused iodide was obtained; the residue proved on analysis to be simply magnesium iodide. It no case was a trace of distillate obtained showing any tendency to fume in the air. The authors point out that magnesium iodide is very hygroscopic, and is so violently acted on by water that they are inclined to think that Hallwachs and Schafarik may possibly have been led to suppose that magnesium ethide in combination was present when really there was only magnesium iodide. Magnesium iodide forms a crystalline compound with ether which apparently has the composition $MgI_2 \cdot 2Et_2O$.

The authors are hence inclined to conclude that previous experimenters have used magnesium containing some impurity which facilitated its action on the iodide; but they do not see reason for assuming that the result was the production of magnesium ethide. They also suggest that possibly the magnesium previously used may have contained zinc, and that small quantities of zinc ethide mixed with hydrocarbons may have been mistaken for magnesium ethide.

The results, however, raise a question of no slight interest. Of the elements of the second natural group, zinc and mercury very readily form compounds with hydrocarbon radicles; cadmium appears to be capable of forming them, though much less readily; and beryllium propide and ethide have been described by Cahours. Calcium, strontium, and barium, on the other hand, presumably do not form such compounds. In which subgroup must magnesium be placed according to this test? Again, aluminium, which follows magnesium in series, forms well-defined compounds with hydrocarbon radicles, while sodium, which precedes it, forms only an unstable double compound with zinc and ethyl. Which does

magnesium resemble, if either? Or has it an intermediate character. It is exceptional for elements on the descending portions of the curve of atomic volumes to unite with hydrocarbon radicles, and a glance at the curve shows that beryllium and magnesium are the only elements undoubtedly occupying such a position that are believed to do so. As to beryllium, it may be pointed out that Cahours (*Comp. Rend.*, lxxvi., 1383) worked with very small quantities and apparently based his conclusions on purely qualitative observations. With regard to magnesium, the authors think that the extremely slight character of the older evidence, and the fact that their own experiments have led to directly contrary conclusions to those of Cahours, justify them in denying its power to form free compounds of the kind discussed. It is, however, just possible that, as indicated by Wanklyn's qualitative experiment, magnesium may form an unstable double ethide with zinc, thus resembling sodium, which immediately precedes it in the natural classification.

DISCUSSION.

Dr. ARMSTRONG said that Messrs. Masson and Wilmore's paper had been despatched from Melbourne on December 29th; meanwhile the question which they had put, and to which they inclined to give a negative reply, had been answered in the affirmative by Löhr in one of the latest numbers of *Liebig's Annalen* (ccxi., 72). Löhr, like the authors, had found that methyl and ethyl iodides had no action at ordinary temperatures either on magnesium alone or on magnesium associated with copper or sodium; and that the action was very sluggish at high temperatures. The presence of a little ethylic acetate served, however, to cause an interaction to set in vigorously in the cold, which was completed within forty to fifty hours at 110°; but the product gave no liquid distillate even at 330°, and Löhr had established the interesting fact that magnesium methide and ethide were solid, non-volatile compounds.

These observations, taken in conjunction with those of the earlier workers in the same field, afforded further evidence that in the formation of organo-metallic compounds, as in so many other cases, it was necessary that some third substance should be present to condition interaction.

Referring to the authors' suggestion, that the magnesium used by previous workers contained zinc, Professor THORPE said that he had had occasion when at the Owens College to analyse a large number of samples of magnesium from Mr. Sonstadt, who, in those days, was the sole maker of the metal, and these never contained zinc, so that he could not agree with the authors in their explanation.

7. "Compounds of the Oxides of Phosphorus with Sulphuric Anhydride." By R. H. ADIE, B.A.

The author has endeavoured to prepare compounds of phosphorus similar to those which the other elements of the group form with sulphuric anhydride.

Employing a preparation obtained from Messrs. Harrington, of Cork, approximately consisting of H_3PO_3 , he obtained, by the action of sulphuric anhydride, a product very nearly of the composition corresponding to the formula $H_3PO_4 \cdot 3SO_3 = (SO_3H)_3PO_4$, in the form of a viscid liquid which was decomposed by water, but without violence, yielding sulphuric and orthophosphoric, and but traces of meta- and pyro-phosphoric acids. Sulphuric anhydride and phosphorus were found to interact violently; the author represents the product by the formula $3P_2O_5 \cdot 2SO_3$. The compound slowly decomposes into phosphoric and sulphurous anhydrides; it is instantly decomposed by water, but the phosphorus containing part dissolves only very slowly.

DISCUSSION.

Professor RAMSAY, after referring to the interest attaching to the investigation of compounds such as were described by the author, expressed the opinion that they were legitimately regarded as salts, and that the existence

of such salts must serve to break down the distinction which was usually made between metals and non-metals based on the formation of salts.

Professor THORPE dissented from this view. He also took occasion to correct the statement made by Mr. Tutton and himself, that the oxide P_4O_6 becomes red on exposure to light; this change, they had since discovered, was due to the presence of a small quantity of phosphorus.

8. "Combustion of Magnesium in Water-Vapour." By G. T. MOODY, D.Sc.

The author points out that the combustion of magnesium in water-vapour, which is very difficult to conduct in the manner commonly described (*cf.* Kessler, *Ber.* ii., 369), may be conveniently demonstrated, as a lecture experiment, by carrying out the operation in a piece of hard glass tube, of about 10 m.m. in diameter, and 250 m.m. in length, bent at an angle of 120° so as to leave one arm nearly twice as long as the other. The shorter arm is inserted through a cork closing the mouth of a "tin can" or other convenient vessel, in which steam can be generated; and the longer arm, which contains a few strips of magnesium ribbon, is connected by a fairly wide delivery tube with the pneumatic trough, at which the liberated hydrogen may be collected. When the air in the apparatus has been displaced by a slow current of steam, the arm in the tube containing the magnesium is cautiously heated by means of a Bunsen burner until the temperature of the tube is considerably higher than that at which water-vapour condenses; the Bunsen burner is then replaced by a blowpipe flame, which is moved about in such a way that the whole of the arm becomes very hot, and on allowing the flame to impinge for a few seconds on a portion of the tube against which the magnesium rests, the metal takes fire and burns with great brilliancy.

The success of this experiment is only assured when there is a *very slow* current of steam passing through the apparatus, and when the tube containing the magnesium is carefully heated, as in the manner above described. Under such circumstances, the metal burns with great regularity, fracture of the tube being usually avoided, and the whole of the hydrogen evolved may be collected.

CHEMICAL SOCIETY'S JUBILEE—1891.

February 24th.

An afternoon meeting took place in the Theatre of the London University, between 3 to 5 o'clock p.m.

The programme included—(1) Introductory speech by the President, Dr. Russell; (2) Address by the Rt. Hon. Sir Wm. Grove, and Address by the Rt. Hon. Sir Lyon Playfair (Original Fellows of the Society); (4) Presentation, by Mr. R. Warrington, of album containing portraits of original Fellows and letters relating to the formation of the Society; (5) Address by Professor Odling on the Development of Chemical Theory since the foundation of the Society; (6) Presentation of addresses from the Royal Society, Pharmaceutical Society, *Société Chimique de Paris*, *Deutsche Chemische Gesellschaft*, and the Russian Physico-Chemical Society; (7) Letters from foreign members.

It is our intention to give a full report of the above proceedings in an early number.

In the evening the Fellows, their friends, and invited guests, to the number of over 1000, were present at a *soirée* at the Goldsmith's Hall, where the following apparatus, specimens, and objects of interest were exhibited.

WILLIAM GILBERT, M.D.,

Author of "De Magnete," founder of the Science of Electricity. Physician to Queen Elizabeth. Born at Colchester, 1540; died, 1603.

This portrait-medallion was executed in clay from the

engraved portrait of Dr. Gilbert, in the studios of the City and Guilds' Technical College, Finsbury, by E. Dunkerley, student, and was electrotyped in copper in the electrical laboratory of the College, by E. Rousseau. Upon the surface of the copper medallion, a layer of metallic cobalt was then deposited by the process invented by Prof. Silvanus P. Thompson.

(Exhibited by Professor Silvanus Thompson).

AMBROSE GODFREY HANCKWITZ (A.D. 1660—1741).

Phosphorus.—This specimen was prepared about the year 1680 by the alchemist, Ambrose Godfrey Hanckwitz, F.R.S., in Robert Boyle's laboratory in Southampton Street, Covent Garden, and is reputed to be a part of the first specimen prepared in this country. For nearly two centuries it remained in the possession of the firm of Messrs. Godfrey and Cooke, which Hanckwitz founded, and in 1876 was presented by them to the Museum of the Pharmaceutical Society.

At the time when this phosphorus was prepared, Hanckwitz was Boyle's assistant, and he obtained it from urine by the method described in Boyle's posthumously published paper (*Phil. Trans.*, 1693). For many years, subsequently, Hanckwitz was the only manufacturer of the substance in Europe. He claims to have been the first to obtain the element in a solid "glacial" form (*phosphorus glacialis urinæ*). In the account (*Phil. Trans.*, 1733), which he gave of his method to the Royal Society in 1733, it is stated "An operator that is not well versed in the degrees of fire, and does not know how and when to take away these oils apart, will have nothing but a volatile salt and fetid oil, and get at least only a little unctuous opaque phosphorus, such as the famous Kunckel, Dr. Krafft, and Brandt did, as they acknowledge in their writings, but not our hard transparent phosphorus."

Engravings.—Two engraved portraits of Hanckwitz, dated 1718 and 1738 respectively.

Three engravings of Robert Boyle's laboratory in Southampton Street, Covent Garden, where Hanckwitz worked. One of these shows the furnaces and retorts used in the preparation of phosphorus. After Boyle's death this laboratory passed into the possession of Hanckwitz, and until the year 1862 was occupied by Messrs. Godfrey and Cooke, who constantly used the original furnaces. The Roman Catholic Church in Maiden Lane, Covent Garden, now stands on the site of the laboratory. These engravings are kindly lent by Joseph Ince, Esq. (Exhibited by Professor Dunstan).

SIR ISAAC NEWTON.

Cupellation furnace, said to have been used by Sir Isaac Newton when Master of the Mint.

(Exhibited by the Science and Art Department, South Kensington).

E. W. SCHEELLE (1742—1786).

Balance in a pocket-case, which belonged to Scheele, who gave it to his pupil Orfila.

(Exhibited by Professor W. H. Corfield).

HENRY CAVENDISH.

Balance used by Cavendish in his chemical and physical investigations.

(Exhibited by the Council of the Royal Institution).

SIR HUMPHRY DAVY.

Balance used by Davy and Young at the Royal Institution.

Galvanic battery used by Davy in the discovery of potassium and sodium.

Specimens which illustrate the experimental development of the miners' safety lamp, as left by Davy at the Royal Institution.

(Exhibited by the Council of the Royal Institution).

THOMAS YOUNG.

Slide rule for Chemical equivalents, constructed for Young.

(Exhibited by the Council of the Royal Institution).

JOHN DALTON.

Apparatus employed by John Dalton in his researches.

The apparatus employed by John Dalton in his classical researches, whether physical or chemical, was of the simplest and even of the rudest character. Most of it was made with his own hands, and that which is exhibited has been chosen as illustrating this fact, and as indicating the genius which, with so insignificant and incomplete an experimental equipment, was able to produce such great results.

Manuscript book containing an account of some of his experiments, in his own handwriting.

Two home-made barometers used by Dalton, consisting of simple syphon tubes with bulbs. One has probably been used for tension experiments.

Graduated glass tube attached to a bottle of india-rubber, probably used in his researches on the absorption of gases in water.

Two phials containing iodine.

Eudiometer.

Gas receiver.

Graduated funnel used probably as gas receiver.

(The Council of the Literary and Philosophical Society Manchester).

SIR JOHN HERSCHEL.

First known photographs on glass taken on precipitated silver chloride, by Sir J. Herschel (Slough, 1839).

"Having precipitated muriate of silver in a very delicately divided state from water very slightly muriated, it was allowed to settle on a glass plate; after forty-eight hours it had formed a film thin enough to bear drawing off the water very slowly by a siphon and drying. Having dried it, I found that it was very little affected by light; but by washing with weak nitrate of silver and drying, it became highly sensible. In this state I took a camera-picture of the telescope on it. Hyposulphite of soda then poured cautiously down washes away the muriate of silver and leaves a beautiful delicate film of silver representing the picture. If, then, the other side of the glass be smoked and black varnished, the effect is much resembling daguerreotype, being dark on white as in nature, and also right and left as in nature, and as if on polished silver."—(Sir J. Herschel; MS. Journal of Chemical Experiments).

(Exhibited by Prof. A. S. Herschel).

Frame of early specimens of the cyanotype and other photographic processes.

(Exhibited by the Science and Art Department, South Kensington).

Photograph of the solar spectrum taken by Dr. Draper, given by him to Sir John Herschel.

(Exhibited by W. Crookes).

J. J. BERZELIUS.

Medallion of Berzelius in selenium. (From the Museum of the Pharmaceutical Society). This was given by Heinrich Rose, of Berlin, to Dr. Theophilus Redwood, then Professor of Chemistry to the Pharmaceutical Society, and one of the early Secretaries of the Chemical Society.

(Exhibited by Professor Dunstan).

A portion of the identical seleniferous deposit in which Berzelius discovered selenium.

(Exhibited by W. Crookes).

MICHAEL FARADAY.

Solutions of gold illustrating the various effects arising from the visibility of gold in a chemical state of division.

Apparatus used by Faraday in the earliest experiments on the liquefaction of gases.

Bar of heavy glass, made and used by Faraday in the discovery of the rotation of the plane of polarisation in the magnetic field.

Specimen of benzole.

Specimen of carbon tetrachloride.

(Exhibited by the Council of the Royal Institution).

THOMAS GRAHAM,

First President of the Society, 1841.

Apparatus employed by Thomas Graham, F.R.S., Professor of Chemistry in University College, and afterwards Master of the Mint, in his principal researches between the years 1834 and 1866.

This series is interesting as showing the simplicity of the appliances with which he discovered laws and facts that have proved of such great importance.

Tubes with discs of graphite and of hydrophane employed by Graham in experiments on the diffusion of gases.

The apparatus employed for ascertaining the diffusion rates of liquids (Bakerian Lecture, 1849).

Osmometers, or apparatus employed in Graham's researches on "Osmotic Force."

Apparatus employed in experiments on liquid diffusion applied to analysis and dialysis.

Apparatus by which Graham studied capillary liquid transpiration in relation to chemical composition.

Tube atmolyser, or instrument for the separation of gases by diffusion.

Barometrical diffusimeter, used for the investigation of the molecular mobility of gases.

Apparatus employed in experiments on absorption and dialytic separation of gases by colloid septa of metal or of india-rubber.

The penetration of metals by gases was studied by the aid of metallic tubes, of which the palladium tube shown is an original one.

(Exhibited by Professor Roberts-Austen, C.B., F.R.S.).

Palladium medal struck by Graham at the Royal Mint, and charged by him with hydrogen. Presented by Graham to the late Dr. Matthiessen.

(Exhibited by the President of the Society).

SIR B. C. BRODIE, BART.,

Secretary to the Chemical Society, 1850—1854;

President of the Chemical Society, 1859—61;

Waynflete Professor of Chemistry, Oxford University, 1855—1872.

Apparatus used in researches on ozone, and the action of electricity on gases, 1860—1872.

Induction tube for producing ozone.

Gas holder for preserving electrified gas over concentrated sulphuric acid.

Measuring pipette. Vol. 290.8 c.c. To deliver a constant volume of electrified gas.

Absorption bulb and aspirator for measuring residual gas after absorption of ozone (calibrated at each of the glass points).

(Exhibited by Dr. W. Odling, Waynflete Professor of Chemistry, Oxford).

DR. GLADSTONE, F.R.S.,

President, 1877—1879.

Hydrate of turpentine, re-crystallised from water. 1846.

Cotton xyloidin. 1847.

Hydrosulphate of menthol. 1865.

Coeruleine, a blue substance found in many essential oils.

DR. GLADSTONE AND THE LATE MR. TRIEB.

Aluminium ethylate, an alcohol substitution product capable of distillation.

$C_{15}H_{10}O$, phenyl ketone produced by heating phenylate of aluminium.

$C_{15}H_{12}O_2$, from a ketone obtained from paracresylate of aluminium.

$C_{15}H_{14}O$, cresyl ketone produced by heating paracresylate of aluminium.
 $C_{15}H_{14}O$, ketone produced by heating thymolate of aluminium.
 $C_{15}H_{14}O$, the above sublimed.
 $C_{10}H_8$, naphthyl ether, obtained from naphthylate of aluminium.
 Isodinaphthyl from a naphthylate of aluminium.
 Chrysene from β -naphthylate of aluminium.
 α -Benzylene obtained from benzyl bromide.
 β -Benzylene obtained from benzyl bromide.
 The original copper-zinc couple.
 The dry copper-zinc couple and its constituents.
 The original air battery.
 Early form of the air battery.

DR. GLADSTONE AND MR. HIBBERT.

Para caoutchouc obtained by precipitation.
 Penang caoutchouc obtained by precipitation.
 $C_{10}H_7Br_3$, action of bromine on caoutchouc.
 (Exhibited by Dr. Gladstone).

WARREN DE LA RUE, D.C.L., F.R.S.,
President, 1867—1869 and 1879—1880.

Photographs of the Moon. One of the earliest applications of photography to celestial physics.

Specimen cells of the great battery of 15,000 cells, used by De la Rue and Müller in their researches on the electrical discharge in gases.

Spark micrometer, for measuring the relation of potential and striking distance.

Tubes used in the study of the electrical discharge in rarefied media.

Voltmeter used in connection with the great battery.
 (From the De la Rue Collection in the Royal Institution).
 Exhibited by the Council of the Royal Institution).

Tyrosine from cochineal.

Carminic acid.

Nitrococcusic acid.

(Exhibited by Dr. Hugo Müller).

(To be continued).

PHYSICAL SOCIETY.

Annual General Meeting, February 13th, 1891.

Prof. A. W. REINOLD, F.R.S., Past President, in the Chair.

THE reports of the Council and Treasurer were read and approved. From the former it appears that there has been a satisfactory increase in the number of members and in the average attendance at the meetings.

During the year a translation of Prof. Van der Waal's memoir on "The Continuity of the Liquid and Gaseous States of Matter" has been issued to members, and it is hoped that the translation of Volta's works, now in hand, will be published before the next General Meeting.

The Council regret the loss by death of Mr. W. H. Snell and Mr. W. Lant Carpenter, and obituary notices of these late members accompany the report.

The Treasurer's statement shows that the financial condition of the Society is very satisfactory, and that the sales of the Society's publications have increased considerably.

A vote of thanks, proposed by Mr. Whipple and seconded by Dr. Gladstone, was unanimously accorded to the Lords of the Committee of Council on Education for the use of the room and apparatus.

Dr. Atkinson proposed a vote of thanks to the auditors, Prof. Fuller and Dr. Fison, which was seconded by Dr. Thompson, and passed unanimously. The proposer, in referring to the satisfactory nature of the accounts, recommended that the publications of the Society should be brought before physicists and other students of physi-

cal science, and Prof. Thompson heartily concurred in this recommendation.

A third unanimous vote of thanks was accorded to the President and Officers for their services during the past year, the proposer and seconder being Dr. Waller and Prof. Minchin.

The following gentlemen were declared duly elected to form the new Council:—

President—Prof. W. E. Ayrton, F.R.S.

Vice-Presidents—Dr. E. Atkinson; Walter Baily, M.A.; Prof. O. J. Lodge, D.Sc., F.R.S.; Prof. S. P. Thompson, D.Sc.

Secretaries—Prof. J. Perry, F.R.S.; T. H. Blakesley M.A., M.Inst.C.E.

Treasurer—Prof. A. W. Rücker, M.A., F.R.S.

Demonstrator—C. V. Boys, F.R.S.

Other Members of Council—Shelford Bidwell, M.A., LL.B., F.R.S.; W. H. Coffin; Maj.-Gen. E. R. Feasting, R.E., F.R.S.; Prof. G. F. Fitzgerald, M.A., F.R.S.; Prof. J. V. Jones, M.A.; Rev. F. J. Smith, M.A.; Prof. W. Stroud, D.Sc.; H. Tomlinson, B.A., F.R.S.; G. M. Whipple, D.Sc.; James Wimshurst.

The meeting was resolved into an Ordinary Science Meeting, and Messrs W. Thorp, B.Sc., G. W. Yule, and S. Joyce were elected members of the Society.

A paper on the "Change in the Absorption Spectrum of Cobalt Glass produced by Heat," by Sir JOHN CONROY, Bart., M.A., was read by Mr. BLAKESLEY.

The absorption spectrum of cobalt glass, when cold, consists of three dark bands in the red, yellow, and green, with a considerable amount of absorption between the first two. When a piece is heated to nearly red heat, the absorption between the first two dark bands diminishes, and the band in the red moves towards the least refrangible end of the spectrum, whilst those in the yellow and green retain their position, but become less distinct. During the heating of the glass the intensity of its colour diminishes, and as the glass cools its original colour and absorption spectrum returns. Diagrams and numbers, showing the character and positions of the bands in hot and cold glass, accompany the paper, together with the numbers obtained by Dr. W. J. Russell (*Proc. Roy. Soc.*, xxii., p. 258) for cold cobalt glass.

In conclusion, the author says that these observations, and those of Feussner on solutions, show that the absorption spectra of some substances vary with temperature. In solutions, this may be due to formation of different hydrates or to partial dissociation, but in a solid, like cobalt glass, an actual change in its chemical constitution at a temperature considerably below its fusing point does not seem probable.

Dr. GLADSTONE said that it was generally known that heat affects the colouring power of substances, and that in solutions absorption is greater the higher the temperature. Different solvents sometimes produce effects analogous to heat; for cobalt salt dissolved in water and in alcohol give pink and blue solutions respectively, and rise of temperature makes the aqueous solution more blue. He concurred with the author as to the causes of the phenomena in liquids, and that the same explanation would not apply to glass.

Prof. S. P. THOMPSON thought Sir John Conroy's results agreed with the experiments which Mr. Ackroyd showed before the Society some years ago, when he demonstrated that the colours reflected by opaque bodies, such as porcelain, &c., when heated, tend towards red.

Prof. MINCHIN showed some experiments in illustration of his paper on "Photo-Electricity," read at the previous meeting.

In one of these, a seleno-aluminium battery, illuminated by the light of a taper, deflected an electrometer needle, thereby actuating a relay and ringing a bell. He afterwards exhibited one of his "impulsion cells" in action, and showed the change from the insensitive to the sensitive state produced by a Hertz oscillator at a distance.

In the discussion, Mr. TUNZELMANN said Kalischer and von Uljanin had worked on the same subject, the former being the first to make experiments on a photo-E.M.F. in selenium. His cells were made by winding brass wire on glass tubes and coating them with selenium, which was subsequently annealed. These cells lost their power after some time, and would not respond to feeble lights. By using two wires of different metals he obtained better results. Fritts, in 1883, used brass and gold plates coated with selenium, and Uljanin employed platinum plates deposited so thin as to be transparent. The latter experimenter found that the E.M.F. was proportional to the square root of the intensity of the light. He also observed that the orange-yellow of the prismatic spectrum produced the greatest effect, whereas the yellow-green and the green rays of the diffraction spectrum gave the maximum E.M.F. Comparing these results with Langley's observations on the distribution of energy in the spectrum, it would appear that the E.M.F. bears no relation to the maximum energy falling on the surfaces. Speaking of the cause of the phenomena, he said the electrolytic idea of von Uljanin seems inapplicable to Prof. Minchin's results, and he enquired whether a mixture of selenium and aluminium would undergo a gradual change by exposure to light.

Dr. GLADSTONE said such a change, if it occurred, would be very slow, for nearly all difficult chemical reactions take time to complete. The fading of colours was adduced as an instance of slow chemical change produced by light.

Dr. WALLER thought the subject might throw light on the changes occurring in the retina, and asked if it was possible to separate thermo-electric and photo-chemical effects.

Dr. BURTON said he had suggested that the action of light on the retina was a photo-chemical one, some time ago. But hitherto it had been difficult to obtain substances sensitive to any but the blue and violet rays, whereas the eye was most sensitive to green and yellow light. In the photo-electric batteries, however, the E.M.F. may generate a current, and, therefore, energy, and the important question seemed to be—Where does this energy come from? Is it a chemical change precipitated by the action of light, or does a direct conversion of light into electrical energy occur?

Prof. MINCHIN, in his reply, said he thought his cells really transformed the incident energy. They were usually kept on open circuit, and there appeared to be no deterioration with time, the only change being a sluggishness in developing their maximum E.M.F.

CORRESPONDENCE.

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To the Editor of the Chemical News.

SIR,—I notice in your last issue (CHEM. NEWS, vol. lxiii., p. 95), a letter from Mr. W. L. Brown, concerning his "Manual of Assaying," and in reply I may say that I was assured (in writing) by the English publisher that he had made the necessary arrangements with the American publishers of the book.

If this had not been so, I can assure Mr. Brown that I would not have edited the book, which I was asked to do by the publisher.—I am, &c.,

A. B. GRIFFITHS.

Constitution of Bone-Meal.—Julius Stoklasa (*Chem. Zeitung*).—Analyses and practical trials made with fine and coarse meals, and with samples rich or poor in grease. Fine meals not containing more than 0.6–1 per cent of grease form a better manure not merely than basic slags, but even than precipitated phosphate.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Moniteur Scientifique, Queneville.

Series 4, Vol. iv., Part 2.

On Beer Yeast. Results of the most Recent Researches and their Industrial Application.—H. Bungener.—This paper requires the numerous accompanying cuts.

Notes on Dyeing.—M. Grandmougin.—These notes comprise an account of the modern method of black dyeing on woollens (*Faerberzeugung*), on the use of the so-called "patent colours" of Croissant and Bretonnière which are useless on woollens; on patent fustine, on dyeing mixed tissues in different colours, on dyeing wool with indulines and on piece-dyeing—all these processes being taken from the *Faerberzeugung*.

Bleaching Wool and Silk with Hydrosulphite.—Gaston Dommergue.

Means of Distinguishing the Resin Oils of the First and Second Distillation.—A. Chenevier.—The author has studied the proportion of acids present in these oils, and makes use of two methods—the gravimetric and the volumetric. He prefers the latter, making use of the process of Burstynn:—To 50 grms. of the oil in a $\frac{1}{2}$ litre flask he adds 100 c.c. of alcohol (at 90° or 95°) and ten drops of an alcoholic solution of rosolic acid at 1 per cent, or five drops of an alcoholic solution of phenolphthaleine at 25 per cent. Then, whilst agitating strongly, he adds with a burette a normal soda, until a permanent red colour is produced. The acidity of the rectified oils rarely reaches 4 per cent, whilst the oils of the first distillation vary from 4 to 10 per cent.

New Practical Method for Detecting Colouring Matters Fraudulently added to Wines.—J. Weirich.—A practical and expeditious method within the reach of all has long been sought for the recognition of wines artificially coloured. The author's method is founded upon the action of air and light upon the colouring matters of wine spread out in an extremely thin layer. The wine is applied with a brush upon a piece of paper of good quality which is not pervious. It is kept for an instant in contact with the paper, which is then drained off and let dry. The colouring matters of wine give the paper a tone quite different from those of the colouring matters—vegetable, animal, or artificial—which serve for the sophistication of wines; the difference is categorical. The natural colours of wine and vegetable colours are transformed upon paper, each according to its nature. The artificial colours are either transformed very slightly or not at all.

New Process for Detecting the Presence of Colouring Matters in Wines.—A. Pagnoul.—The process depends on the property of soap-lyes to destroy the natural colouring matter of wines without giving them the greenish tint communicated by other alkaline solutions, and without affecting strange colours.

Another Process for Detecting Foreign Colouring Matters in Wine.—L. Sostigni (*Chem. Central Blatt*).—Foreign colouring-matters which are not decomposed by alkalis at an ordinary temperature (e.g., safranine, eosine, &c.), or which they turn to a violet (e.g., the tropaeolines and cochineal), may be easily detected as follows. The wine is treated with 1-10th of its volume of a solution of potassa at 10 per cent, shaken up for five minutes, and the liquid poured into a filter of parchment paper, in contact externally with water. After some hours a yellow liquid containing the oxidation products of the tannin is diffused. This result is complete in twenty-four hours, or in forty-eight hours in case of

wines very rich in tannin. The colouring matters foreign to wine are fixed upon the parchment paper with their own colours. Natural wines colour the paper yellow.

Analyses of Concentrated Superphosphates.—J. Hughes (*Chemiker Zeitung*).—Iron and aluminium phosphates are insoluble in water, but soluble in a strong solution of super phosphate. When we extract the soluble phosphoric acid from superphosphates, it is of the greatest importance to use a sufficient quantity of water for the first extraction. Otherwise, the quantity of soluble phosphoric acid may be found too high by 1 to 2 per cent.

Manufacture of Ammoniacal Manures.—Gahn and Barte (German Patent, No. 47601), pass ammoniacal vapours into troughs containing acid phosphates. The ammonia is obtained from gas-liquor by means of lime.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Detection of Sulphites in Presence of Thiosulphates and Sulphides.—Will any reader of the *CHEMICAL NEWS* inform writer where details of this test—mentioned in Fresenius's "Qualitative," 8th English Edition, pp. 174-175, and there attributed to Bödeker—are to be found. Reference to original publication containing details of reaction of sulphides with sodic nitroprusside would assist writer.—*THURON*.

MEETINGS FOR THE WEEK.

- MONDAY, Mar. 2nd.**—Medical, 8.30. (Annual Meeting).
— Royal Institution, 5. General Monthly Meeting.
— Royal Medical and Chirurgical, 8.30. (Anniversary).
— Society of Arts, 8. "The Electric Transmission of Power," by Giabert Kapp.
— Society of Chemical Industry, 8. "The Chemical Changes between Nitric Acid and Metals," by V. H. Veley. "Further Researches on the Butter of the Cow," by J. A. Wanklyn.
TUESDAY, 3rd.—Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley, F.R.S.
WEDNESDAY, 4th.—Society of Arts, 8. "Modern Flour Milling," by J. Harrison Carter.
THURSDAY, 5th.—Royal, 4.30.
— Royal Society Club, 6.30.
— Chemical, 8.
— Royal Institution, 3. "Modern Chemistry in Relation to Sanitation," by Professor C. Meymout Tidley.
FRIDAY, 6th.—Royal Institution, 9. "Electromagnetic Repulsion," by Prof. J. A. Fleming.
— Society of Arts, 4.30. "The Science of Colour," by Captain Abney.
— Geologists' Association, 8.
— Quakers, 8.
— Physical, 5.
SATURDAY, 7th.—Royal Institution, 3. "The Forces of Cohesion," by The Right Hon. Lord Rayleigh, F.R.S.
— Medical, 8.30. (Annual Dinner).

TO CORRESPONDENTS.

Spectroscope.—Paper washed with a weak solution of chloride of cobalt changes colour according to the dryness or humidity of the atmosphere.

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Chemical News, COMPLETE SET, 1860 to 1888; 58 vols. cl., £20.
Chemistry applied to Arts and Manufactures by writers of eminence (Schorlemmer and others); engravings, 8 vols. (1880), £4. for 43s.
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THE CHEMICAL NEWS.

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ON THE TRANSITION OF CERTAIN PRECIPITATES FROM THE AMORPHOUS TO THE CRYSTALLINE STATE.

By GEORGE WATSON, F.C.S.

A NUMBER of precipitates are known which, when newly thrown down from a solution, are amorphous, but which, on standing in contact with the liquid in which they have been formed, pass more or less rapidly into the crystalline state.

Thus, for example, antimonious chloride, when added to water, gives at first a bulky amorphous precipitate of basic antimonious chloride. On standing, however, and especially if well stirred, this precipitate changes into a heavy crystalline powder. So also calcic carbonate, when formed from a watery solution of calcic chloride, by the addition thereto of an alkaline carbonate, is, when newly formed, amorphous and somewhat bulky, but soon changes, at temperatures below 30° C., into crystals of calc spar. If, on the contrary, the liquid containing the amorphous precipitate be heated to the boiling-point, crystals of "arragonite" are said to be produced. Several other cases of a similar nature might be instanced.

On considering such cases the questions naturally arise in the mind, why does this change take place? and what is the method of working according to which it proceeds? Hence, having examined a few of them, and having obtained what seemed to me to be satisfactory answers to the above questions, I thought my results might be of sufficient interest to place on record.

Consider first the case of basic antimonious chloride. If some antimonious chloride solution be added to water there is obtained the well-known bulky precipitate of basic antimonious chloride, which changes, on standing, into a heavy crystalline powder. If, while it is still amorphous, a number of scratches be made on the surface of the glass in contact with the precipitate, these scratches will be found to be covered with attached crystalline precipitate after the change from the amorphous to the crystalline state has taken place. If the scratches be washed with hydric chloride and again put in contact with a new quantity of amorphous precipitate, no fixation is now found to have occurred after the transition has happened. But if, on the other hand, scratches with adhering crystalline precipitate be again placed in contact with a new quantity of the amorphous form, the deposit is found to increase in amount. This latter result shows that the crystalline modification influences favourably this change from the amorphous to the crystalline state. In other words, the change, in one respect at least, is an accelerating one. This may be seen by forming a quantity of the amorphous precipitate in admixture with a pre-formed quantity of the crystalline one, and comparing the speed with which the change now proceeds with that of a parallel experiment to which no pre-formed crystalline precipitate has been added. It will be found that the former rapidly settles to the bottom of the glass, while the latter still remains suspended in the amorphous form.

These facts were recorded in a paper which I published in the CHEMICAL NEWS, vol. lxi., p. 207. At that time I thought that this fixation of precipitate on the abrasions took place directly from the amorphous precipitate lying contiguous to them; but since then I have examined the matter more minutely, and now find that it occurs from the acid liquid in which the precipitate is suspended, and

that the way in which the change from the amorphous to the crystalline state takes place is as follows:—

The precipitation of basic antimonious chloride by water occurs in two stages. In the first stage, the bulk of the antimony is thrown down as amorphous, basic, antimonious chloride. A small quantity, however, remains in solution, constituting, as it were, a saturated solution of amorphous basic antimonious chloride, but a supersaturated one if regarded as a solution of the crystalline basic salt. In the second stage this small quantity of basic chloride is deposited in the crystalline state, and attaches itself to any scratches which may be made on the glass. But simultaneously with this deposition a new quantity of the amorphous precipitate has again gone into solution, the amorphous precipitate being more soluble in hydric chloride than is the crystalline form. Supersaturation is therefore maintained, and the previously deposited crystals now act on this solution and hasten the formation of the next quantity of crystal. The process of alternate re-solution and re-precipitation thus proceeds until the change is complete.

The following are the experiments on which this explanation is based:—

A solution of antimonious chloride was made by dissolving 2 ounces of crystallised antimonious chloride in 50 c.c. of water and 25 c.c. strong hydric chloride (1:160).

1. To 100 c.c. water were then added 5 c.c. of this solution, the mixture stirred well, and 20 c.c. at once filtered off. On diluting this 20 c.c. with water and gassing with hydric sulphide, a considerable precipitate, comparatively speaking, of antimonious sulphide was obtained. The basic antimony chloride precipitate was then allowed to change into the crystalline state and other 20 c.c. of the supernatant filtered off and gassed with hydric sulphide, when a mere trace only of antimonious sulphide was obtained.

2. To 200 c.c. water were added 10 c.c. antimony solution, the whole stirred up, and the liquid at once filtered into a clean, dry test-glass. The filtrate, on standing twenty-four hours, deposited a precipitate of crystalline basic antimonious chloride.

3. 100 c.c. water and 5 c.c. antimony solution were mixed, and 21 c.c. strong hydric chloride run in from a burette with continuous stirring. The precipitate slowly dissolved and gave a milky solution, which, on filtration, yielded a clear liquid. On stirring this clear liquid vigorously, a precipitate came down which increased greatly on standing. The addition of even 24 c.c. of hydric chloride to a similar liquid in which the precipitate had become crystalline failed to effect complete solution in two days' time.

That this change takes place as described is also supported by the fact that if the amorphous precipitate be rapidly separated from the liquid, and all water removed by washing with ether, it may be obtained in that form and preserved indefinitely. (See Roscoe and Schorlemmer's "Treatise on Chemistry," vol. ii., Part 2, p. 317).

But it follows from what has been said that until the small quantity of antimony in the supernatant has crystallised out, the change of the already formed amorphous precipitate into the crystalline state cannot take place, a conclusion which shows us how this substance could be used as a substitute for tartar emetic in fixing coal-tar colours on cotton. For, if a piece of cotton impregnated with tannin were immersed in the emulsion, the small quantity of antimony in solution would be withdrawn and fixed as tannate on the fabric. A new quantity of antimony would then go into solution, only to be withdrawn and fixed on the cotton, and, theoretically, this process could go on until all the antimony had become re-dissolved, withdrawn from solution, and fixed as tannate on the cotton fibres. This substance, therefore, should form a very cheap substitute for tartar emetic and the other antimony salts used for this purpose—a conclusion

supported by a statement in the *Journal of the Society of Chemical Industry* for 1885, vol. iv., p. 644.

Another antimonious precipitate which also undergoes a change from the amorphous to the crystalline state in the way already described for the basic chloride is sodic antimoniate. This precipitate, when at first formed in solutions strong enough to give an immediate precipitation, is somewhat bulky and amorphous, but on standing changes comparatively quickly into the crystalline state. In this case also the precipitation takes place in two stages, depending on the greater solubility of the amorphous form as compared with the crystalline one.

In the first stage the bulk of the precipitate is thrown down in the amorphous condition, while in the second the small remainder comes down, but in the crystalline form. If the solution be sufficiently dilute, however, the first stage is eliminated and all the precipitate slowly appears in the crystalline state. In the case of this precipitate also, when formed in strong solutions, the phenomena of attaching itself to abrasions and of acceleration in the rate of change are exhibited, both of which are indications that we are dealing with a solution having the properties of a supersaturated one. In my experiments with this substance I used solutions consisting of 10 c.c. of saturated solution of sodic chloride mixed with 100 c.c. of water, to which were added 25 c.c. of a boiling saturated solution of potassic antimoniate.

Another precipitate which changes from the amorphous to the crystalline state by the process of alternate resolution and re-precipitation is monocalcic orthophosphate (CaHPO_4)—the precipitate obtained by mixing solutions of calcic chloride and disodic phosphate. Thus, if 50 c.c. water, 25 c.c. of a cold saturated solution of disodic phosphate, and 15 c.c. of a 5 per cent solution of calcic chloride be mixed, a white gelatinous precipitate of monocalcic phosphate is obtained. On scratching the glass in contact with the precipitate with a pointed glass rod, such scratches are found to be coated with crystalline precipitate after the change has taken place. Also, if the supernatant be at once filtered off it deposits a further small quantity of precipitate in the crystalline state, and if the amorphous form be produced in admixture with a pre-formed quantity of the crystalline modification, the change from the one form to the other, as evidenced by the rapidity with which the precipitate settles, is found to take place much more rapidly.

Yet another instance of change from the amorphous to the crystalline state, by the process of alternate resolution and re-precipitation, is seen in the case of calcic carbonate. This substance when at first precipitated from a cold solution of calcic chloride by means of an alkaline carbonate is amorphous, but changes on standing at ordinary temperatures into crystals of calc spar. On heating the liquid containing the amorphous precipitate it is said to be transformed into crystals of "aragonite."

The following are my experiments with this precipitate:—

To 60 c.c. of a 5 per cent solution of pure calcic chloride were added 20 c.c. of a 10 per cent solution of sodic carbonate, and the glass in contact with the precipitate abraded with a pointed glass rod. After the change into the crystalline form had taken place, the abrasions were found to be heavily laden with precipitate—a criterion that we are dealing with a supersaturated solution, and therefore that this precipitation also occurs in two stages. In the first, the bulk of the precipitate is thrown down amorphous, while in the second the small remainder crystallises out as "calc spar" or "aragonite," according as the temperature of the solution is low or high.

In this case also, by forming the amorphous modification in admixture with a pre-formed quantity of the "calc spar" form, the fact of acceleration in the rate of change is seen, as evidenced by the rapidity with which the pre-

cipitate settles as compared with a parallel precipitate unmixed with pre-formed "calc spar."

Experiments to ascertain if this greater solubility of the amorphous modification were due to dissolved carbon dioxide in the solution, showed that the change took place equally in ammoniacal and in boiled solutions. The change, in this case at any rate, is therefore due to the greater solubility of the amorphous calcic carbonate in solutions of sodic chloride. The solubility of this substance has also been observed by Sterry Hunt (*CHEMICAL NEWS*, vol. lxii., p. 319).

This change from the amorphous to the crystalline state in the case of calcic carbonate is the cause of the hardening or setting of ordinary mortar, in so far as this is due to the absorption of carbon dioxide. A quantity of calc spar crystals are thus formed which, interlacing with the sand, bind it into a mass of some tenacity, in the same way that a moist powdered salt, such as sodic chloride, when dried gives a cake of more or less coherency, due to the formation of interstitial crystals which interlace with the rest of the salt and bind it together.

It may be of interest to notice here also two other cases which have been examined by other chemists. The first is the transformation of arsenious oxide from the vitreous to the crystalline state, observed when a mass of the former variety is kept for some time exposed to the air. This change has been investigated by C. Winkler (*Journ. Prakt. Chem.* [2] vol. xxxi., p. 247, abst. in *Chem. Soc. Journ.*, 1885, p. 871), who found that the crystalline variety formed from the vitreous form by keeping always contained a small quantity of water, and who, therefore, surmised that the change was caused by this water and was owing to the greater solubility of the vitreous form—a conclusion which he verified by experiment. The other instance is the change of calcic sulphate from the amorphous anhydrous to the crystalline hydrated condition, a change which constitutes the phenomenon known as the "setting" of plaster-of-Paris. This change has been examined by H. Le Chatelier (*Comptes Rendus*, vol. xcvi., p. 715—718, abst. *Chem. Soc. Journ.*, 1883, vol. xlv., p. 712), according to whom the setting of plaster-of-Paris is due to the formation of an agglomerate of interlacing crystals of hydrated calcic sulphate, produced from the amorphous sulphate by a process of solution and crystallisation and conditioned by the greater solubility of the amorphous form as compared with the crystalline one. But from what has already been said it is evident that this change also must proceed at an accelerating rate, so far as the withdrawal of the hydrated calcic sulphate from solution is concerned, although this does not seem to have been noticed by Le Chatelier. This may be seen in the following way. Take 10 grms. of plaster-of-Paris, mix it with 10 c.c. of water, and allow some of the resulting liquid to run out of a pipette on a slab of "set" plaster. Each drop as it falls on the slab at once congeals into the solid state. Or, take a drop on the end of a glass rod and touch the slab with it, when it will congeal and adhere to the slab. On touching this congealed drop with a fresh one, the latter also congeals and adheres to the former, and by continuing this process it is possible to build up a little cone of congealed plaster, while the rest of the mixture still remains liquid.

In conclusion there is one other point to which I would refer. Inasmuch as calcic carbonate is dimorphous, one would conjecture that it should be possible to cause the gelatinous amorphous form of this substance to turn into the form of aragonite crystals at ordinary temperatures (below 30° C.), by introducing a quantity of these crystals into the liquid. In order to see if this were so, three samples of calcic carbonate were prepared; (a) by precipitating 2 litres of lime water at the boiling-point by a stream of carbon dioxide; (b) same as above, but precipitated in the cold (8° C.); (c) by precipitating 1 litre at the boiling-point, cooling, pouring off the liquid, and adding the aragonite crystals thus obtained to another litre of lime water, which was then precipitated in the cold

by carbon dioxide. The resulting precipitates were then washed, dried, and their specific gravities taken, with the following results:—

A	2.642	water at 8° C.
B	2.676	"
C	2.646	"

As these figures are practically identical, and are, in fact, the same as the specific gravity of calc spar, it is impossible to draw any definite conclusion from them. I am therefore now engaged in further experiments to examine this point more minutely, and likewise to determine to what extent, and at what rate, "arragonite" crystals revert to the form of "calc spar" on standing in contact with water.

ESTIMATION OF GLYCERIN BY ALKALINE PERMANGANATE.

By WILLIAM JOHNSTONE, D.Sc.

ON the 16th inst. I had the honour to read a paper before the Society of Chemical Industry upon the above subject.

The experiments were undertaken owing to Professor Wanklyn having expressed to me a doubt as to whether butyric acid could not be converted into oxalic acid by boiling with alkaline permanganate. Known quantities of butyric acid were therefore taken and boiled with alkaline permanganate, and to my great astonishment, and contrary to the statements of Benedict and Zsigmondy, I obtained 94 per cent of the butyric acid originally taken, calculating it from the oxalic acid found.

The following equation apparently represents the reaction:— $C_4H_6O_2 + O_6 = 2C_2H_2O_4 + H_4$. The acid used has been boiled with dilute sulphuric acid and bichromate of potash for six hours without any alteration; consequently the sample was free from any iso acid, which might have interfered with the accuracy of the results obtained.

Mr. Allen's improved method of Benedict and Zsigmondy's process (*Four. Chem. Soc. Ind.*, vol. v., p. 70), is therefore utterly inapplicable for the estimation of glycerin in oils and fats containing butyric acid.

A GENERAL METHOD FOR THE ANALYSIS OF THE BRANDIES AND ALCOHOLS OF COMMERCE.

By M. ED. MOHLER.

IN the spirits of commerce we have already methods for determining extract, alcohol, acids, and furfural. The method now described renders it possible in half-litre samples to determine also the ethers, the aldehyds, the higher alcohols, and the nitrogenous products. These determinations have to be made on the distilled liquid brought to the standard of 50°, except as regards the nitrogenous products, which are determined in the sample itself.

Determination of Ethers.—The author boils 100 c.c. of the distilled alcohol for an hour along with 20 c.c. of decinormal potassa, the flask being fitted with an ascending condenser. The quantity of potassa absorbed is calculated by taking account of the acidity of the alcohol, and the results are calculated as ethyl acetate.

Aldehyds.—The intensity of the violet colour developed by the action of rosaniline bisulphite upon alcohols containing aldehyds is not proportional to the quantity in solution. To apply this reagent to the determination of the aldehyds it must be caused to act upon a solution of known strength, and to bring the alcohol to be

analysed by dilution to contain a quantity of aldehyd equal to that of the standard.

To 10 c.c. of a solution of ethylic aldehyd at 100° and to 10 c.c. of the alcohol under analysis (both at 50° of alcoholometric strength) we add at the same time 4 c.c. of rosaniline bisulphite. The tints are allowed to develop for twenty minutes, and their intensity is then compared by means of the Duboscq colorimeter. The operation is re-commenced by diluting the alcohol in question until the colours have the same intensity. If *m* represents this dilution, the weight of ethylic aldehyd per litre will be $M \times 0.050$.

Higher Alcohols.—Sulphuric acid in the conditions in which it is employed acts only on the aldehyds and the higher alcohols. The aldehyds are kept back by means of aldehyd phosphate.

To 100 c.c. of the distilled sample we add 1 c.c. of aniline and 1 c.c. of phosphoric acid at 45° B. The liquid is boiled for an hour with an ascending condenser, and is then distilled to dryness in a salt-bath.

The distillate is treated with sulphuric acid at 66° according to the known method, and the tint observed is examined comparatively in the colorimeter with that given by an alcoholic solution containing 0.250 isobutylic alcohol per litre.

We operate, as in the case of the alcohols, by diluting the alcohol until the tints are equalised.

Nitrogenous Products.—We have determined the weight of ammonia corresponding on the one hand to the amides and to saline ammonia, and on the other to the pyridic bases and the alkaloids, by submitting the alcohol in question first to the action of sodium carbonate and then to that of alkaline permanganate, titrating the small quantities of ammonia produced in each operation with Nessler's reagent.

To 100 c.c. of the sample not distilled we add 2 c.c. of phosphoric acid at 45° B., and expel all the alcohol by boiling. The phosphoric solution of the bases is diluted with about 1 litre distilled water; 10 grms. of pure sodium carbonate are added, and the mixture is distilled until no more ammonia passes over. The permanganate and the potassa are then introduced, and the distillation is continued, the ammoniacal water being collected in another receiver. The ammonia obtained from each operation is determined with Nessler's reagent comparatively with a solution containing 0.00001 gm. ammonium hydrochlorate per c.c.

The method just described permits us to analyse in samples of 500 c.c. alcohol containing not more than 1.200,000th of acids, 1.200,000th of ethers, 1.1,000,000th of ethers, 1.1,000,000th of furfural, 1.20,000th of higher alcohols, and 1.100,000th on operating with alcohol at 90°, 1.1,000,000th of ammonia corresponding to saline ammonia and amides, and 1.10,000,000th of ammonia corresponding to the alkaloids and to pyridic traces.—*Comptes Rendus*.

Observations by M. Edm. Becquerel on M. Lippmann's Communication concerning the Photographic Reproduction of Colours.—The author points out the distinction existing between the purely physical process which M. Lippmann has just expounded for the photographic reproduction of the colours of light and the photo-chemical process which the speaker discovered in 1848 for obtaining the coloured images of the luminous spectrum as well as the images of objects with their own colours, that is by means of one and the same chemical substance, argentous chloride. This matter possesses the curious attribute, when properly prepared, of being not merely sensitive to the action of the coloured rays from the red to the violet, but also of receiving an impression which seems sensibly proportional to the intensity of the corresponding luminous impressions upon the retina.—*Comptes Rendus*, Vol. cxii., No. 5.

ELECTRICITY IN TRANSITU: FROM PLENUM TO VACUUM.*

By WILLIAM CROOKES, F.R.S.,
President of the Institution of Electrical Engineers.

(Concluded from p. 100).

What Occasions Phosphorescence?

I SHOULD like to interest you in a question that has exercised my mind for some time past. What is it that occasions the phosphorescence of yttria and other bodies in vacuo under molecular bombardment?

So far I have found this phosphorescence to be an attribute of non-conductors only. We know that in the act of phosphorescence the molecules of yttria are in a state of intense vibration. Each molecule may be viewed as the radiating centre of the entire bundle of rays, which, when decomposed by the prism, displays a discontinuous spectrum. We may also suppose that the residual atoms of gas charged with negative electricity give off their electricity on coming in collision with a phosphorescent body, and on their return take up a fresh charge.

The Electrolysis Hypothesis.

There is a certain amount of evidence in favour of an electrolytic hypothesis of the passage of electricity through rarefied gases. This has been ably advocated by Professor Schuster in the Bakerian Lecture before the Royal Society, March 20th, 1890.†

A molecule of hydrogen gas, for instance, may be made up of one group of atoms of hydrogen having an equivalent of negative electricity inherent in it, and one group of atoms having an equivalent of positive electricity bound up with it. These atoms are also charged with *additional* equivalents of positive or negative electricity, which they carry about as a ship carries its cargo. We are not concerned with the inherent electricity—of which we are ignorant—but with the extra or “cargo” charge. Let us imagine a molecule of hydrogen near the face of the negative pole in a vacuum tube. I turn on the current, and the atoms of the hydrogen molecule are dragged apart. The positive atom is attracted to the negative pole, where the violence of impact, or the discharge of electricity, renders it apparent with evolution of light. The internal luminous layer, which is closely adjacent to the negative electrode, is due, therefore, to the positive atoms rushing to the negative pole, and not, like the glow round the edge of the dark space, to the negative atoms projected from it. The negative atom, on the other hand, is driven violently from the negative pole, in virtue of the mutual repulsion existing between any two bodies similarly electrified, with a velocity varying with the intensity of the electrification and the degree of the vacuum; the more perfect the vacuum the greater the velocity, the atoms flying outwards in straight lines until they meet with an obstacle. Such an obstacle may be a procession of positively charged atoms from the positive pole; in this case the two kinds of atoms mutually discharge each other's cargos with a display of light. This phenomenon occurs at the margin of the dark space when the vacuum is only moderate. Or the obstacle may be produced by the vacuum being so high that the atoms of gas present are too few to form a continuous procession. (Why a high vacuum should be non-conductive does not clearly appear, but the fact itself is beyond doubt; it is probably connected with the inability of electrified atoms to leave the poles.) Or again, the obstacle may be a phosphorescent body like yttria. In this case the negatively charged atoms deliver up their charge of electricity to the yttria, which is so constituted—perhaps after the manner of a Hertz resonator—that its atoms charge and discharge, vibrating about 550 billion

times in a second, and producing waves in the ether of the length, approximately, of 574 ten-millionths of a millimetre, and occasioning in the eye the effect of citron light.

We are not under the necessity of supposing that this number of hydrogen atoms are driven against the yttria in the second, although even at a high vacuum there are quite enough atoms left in the bulb to keep up such a supply. All that is needed is that a succession of shocks, not necessarily rhythmical, may strike the yttria at frequencies which will set up such a number of vibrations, just as a series of slow impacts on a gong causes it to emit sound waves of much greater frequency.

In a low vacuum only very few atoms can run the gauntlet among the crowd of intruding atoms, and those few which succeed in reaching the yttria arrive with much reduced velocity, and so faint is the phosphorescence they set up that it is completely obscured* by the brighter phosphorescence of the residual gas. As the vacuum becomes higher, more and more atoms find their way across, and their speed being at the same time accelerated, the phosphorescence becomes intensified.

At a good vacuum most of the atoms hit the yttria, their velocity is increased, and the rhythmical excitation reaches its maximum.

The Dark Space in Mercury Vapour.

In applying the electrolytic hypothesis, I have used for illustration's sake the gaseous residue of hydrogen, which is known as a diatomic gas. I have found, however, the phenomena of the dark space, &c., to occur in the vapour of mercury, which is a monatomic gas. This important result induced me to patiently investigate this subject, and the result of one experiment is before you (Fig. 29). The tube is furnished with aluminium terminals, and is so arranged that the induction spark can be kept passing during exhaustion to drive off occluded gases. When at the highest attainable vacuum, the tube is filled with pure mercury by simply raising a reservoir. On applying heat the entire contents of the tube are boiled away and pass down the fall tubes of the pump, exhaustion going on at the same time. When the whole of the mercury has thus been boiled away *in vacuo*, except a little condensed at the upper part of the tube, the results on passing the spark are as follows:—When the tube is cold the induction current refuses to pass; on gently heating with a gas-burner the current passes and the dark space is distinctly visible. Continuing the heat so as to volatilise the drops of mercury condensed on the sides, the whole tube becomes filled with a green phosphorescent light, the dark space gets smaller and smaller, and ultimately the negative pole becomes covered with a luminous glow. On allowing the tube to cool the same phenomena ensue in inverse order. The luminous halo expands, showing the dark space between it and the pole, and this dark space gradually grows larger as the tube becomes cooler. The mercury again condenses on the side of the tube, the green phosphorescence grows paler and paler, until at last the induction spark from the large coil refuses to pass.

At first sight this result appears fatal to the electrolytic hypothesis, for if the molecule of mercury contains only one atom how can we talk of its separation into positive and negative atoms by the electric stress? It must be remembered, however, that we are as yet ignorant of the absolute mass of the atom of any element. All that can be said is that a molecule of free hydrogen becomes halved in combining chemically with certain other elements, whilst a molecule of free mercury does not suffer division on yielding any known compound of mercury: the physical atoms in the one behave as two separate groups, and those in the other as one undivided group. It has been agreed by chemists, for simplicity's sake and for facili-

* Inaugural Address delivered January 15th, 1891.

† Roy. Soc. Proc., xlvii, 526.

* This faint phosphorescence at a low vacuum can be rendered visible by the electrical phosphoroscope described in my lecture at the Royal Institution in 1887.

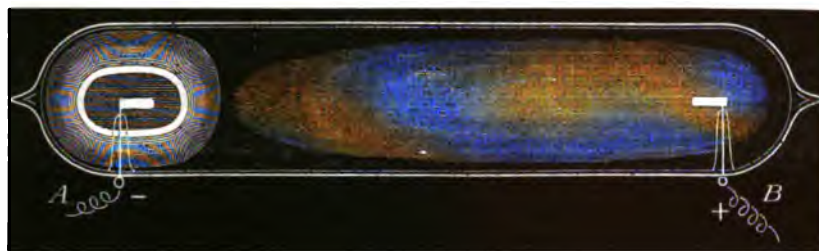


FIG. 29.

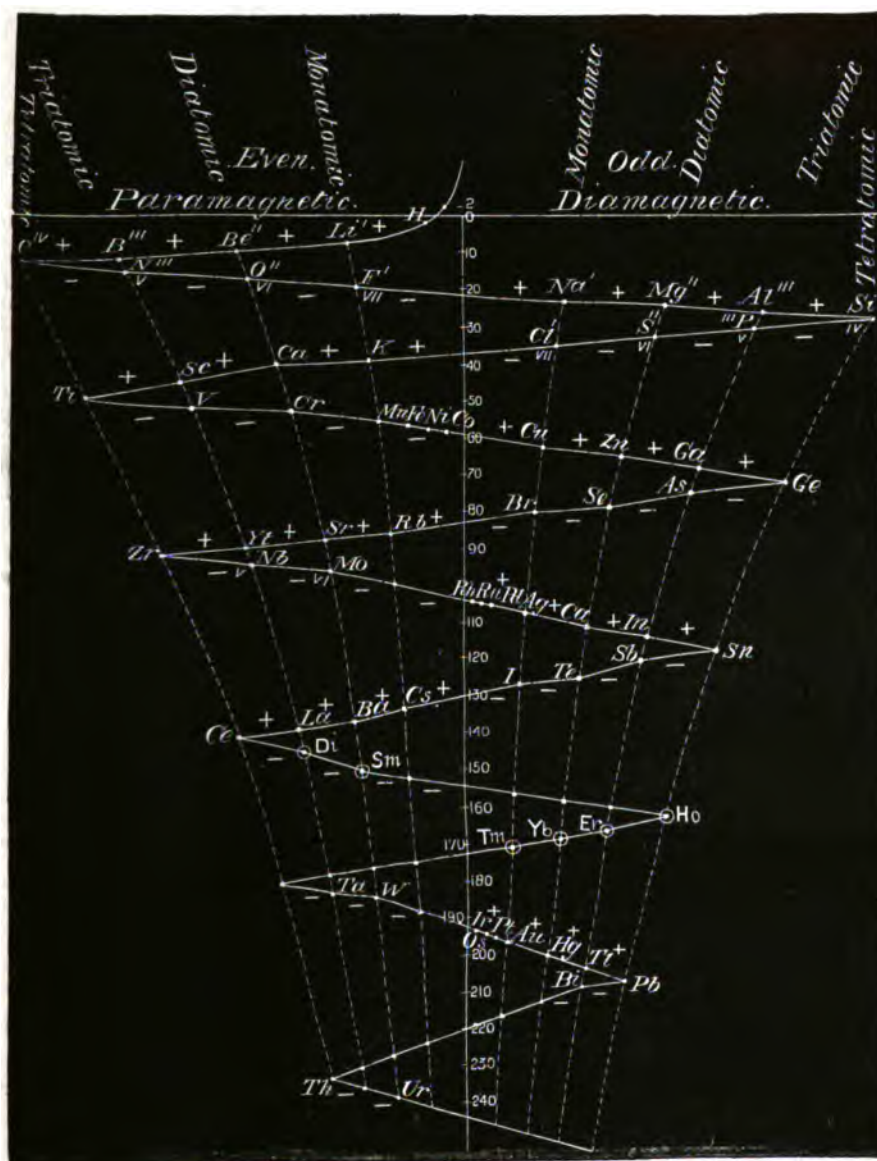


FIG. 30.

tating chemical calculations, to reduce the units to the lowest term, consistent with the avoidance of fractions; we therefore say that the atoms in a molecule of free hydrogen act in chemistry as two separate groups, each of a minimum relative weight of 1, whilst those in a molecule of free mercury act as one undivided group of the relative weight 200. But to what number of atoms the 1 and 200 correspond respectively no chemist knows.

To show how intimately chemistry and electricity interlock, I may here remark that one of the latest theories in chemistry renders such a division of the molecule into groups of electro-positive and electro-negative atoms necessary for a consistent explanation of the genesis of the elements. This is so important that I may be excused for digressing a little into this development of theoretical chemistry.

Genesis of the Elements.

It is now generally acknowledged that there are several ranks in the elemental hierarchy, and that besides the well-defined groups of chemical elements, there are underlying sub-groups. To these sub-groups has been given the name of meta-elements. The original genesis of atoms assumes the action of two forms of energy working in time and space—one operating uniformly in accordance with a continuous fall of temperature, and the other having periodic cycles of ebb and swell, and intimately connected with the energy of electricity (Fig. 30). The centre of this creative force in its journey through space scattered seeds or sub-atoms that ultimately coalesced into the groupings known as chemical elements. At this genetic stage the new born particles vibrating in all directions and with all velocities, the faster moving ones would still overtake the laggards, the slower would obstruct the quicker, and we should have groups formed in different parts of space. The constituents of each group whose form of energy governing atomic weight was not in accord with the mean rate of the bulk of the components of that group, would work to the outside and be thrown off to find other groups with which they were more in harmony. In time a condition of stability would be established, and we should have our present series of chemical elements each with a definite atomic weight—definite on account of its being the average weight of an enormous number of sub-atoms or meta-elements, each very near to the mean. The atomic weight of mercury, for instance, is called 200, but the atom of mercury, as we know it, is assumed to be made up of an enormous number of sub-atoms, each of which may vary slightly round the mean number 200 as a centre.

We are sometimes asked why, if the elements have been evolved, we never see one of them transformed, or in process of transformation, into another? The question is as futile as the cavil that in the organic world we never see a horse metamorphosed into a cow. Before copper, e.g., can be transmuted into gold it would have to be carried back to a simpler and more primitive state of matter, and then, so to speak, shunted on to the track which leads to gold.

This atomic scheme postulates a to and fro motion of a form of energy governing the electrical state of the atom. It is found that those elements generated as they approach the central position are electro-positive, and those on the retreat from this position are electro-negative. Moreover the degree of positiveness or negativeness depends on the distance of the element from the central line; hence calling the atom in the mean position electrically neutral, those sub-atoms which are on one side of the mean will be charged with positive electricity, and those on the other side of the mean position will be charged with negative electricity, the whole atom being neutral.

This is not a mere hypothesis, but may take the rank of a theory. It has been experimentally verified as far as possible with so baffling an enigma. Long-continued research in the laboratory has shown that in matter which has responded to every test of an element, there are minute shades of difference which have admitted of

selection and resolution into meta-elements, having exactly the properties required by theory. The earth yttria, which has been of such value in these electrical researches as a test of negatively excited atoms, is of no less interest in chemistry, having been the first body in which the existence of this sub-group of meta-elements was demonstrated.

Conclusion.

I frankly admit I have by no means exhausted the subject which daily and nightly fills my thoughts. I have ardently sought for facts on which to base my theory. I have struggled with problems which must be conquered before we can arrive at exact conclusions—conclusions which, so far as inorganic Nature is concerned, can only be reached by the harmonious interfusion—not confusion—of our present twin sciences, electricity and chemistry. Of this interfusion I have just endeavoured to give you a foretaste. In elaborating the higher physics, the study of electrical phenomena must take a large, perhaps the largest, share.

We have invaded regions once unknown, but a formidable amount of hard work remains to be completed. As we proceed we may look to electricity not only to aid, as it already does, our sense of hearing, but to sharpen and develop other powers of perception.

Science has emerged from its childish days. It has shed many delusions and impostures. It has discarded magic, alchemy, and astrology. And certain pseudo-applications of electricity, with which the present Institution is little concerned, in their turn will pass into oblivion.

There is no occasion to be disheartened at the apparent slow pace of elemental discovery. The desponding declare that if Roger Bacon could re-visit "the glimpses of the moon" he would shake his head to think we have got no further, that we are still in a haze as to the evolution of atoms. As for myself I hold the firm conviction that unflinching research will be rewarded by an insight into natural mysteries such as now can scarcely be conceived. Difficulties, said a keen old statesman, are things to be overcome, and to my thinking Science should disdain the notion of Finality. There is no stopping half way, and we are resistlessly driven to ceaseless inquiry by the spirit "that impels all thinking things, all objects of all thought, and rolls through all things."

DETERMINATION OF WATER IN SUPERPHOSPHATES.*

By JULIUS STOKLASA.

(Continued from p. 101).

If the phosphoric anhydride corresponding to the free phosphoric acid is deducted from the 35.8 per cent P_2O_5 found, we have 29.2 per cent P_2O_5 corresponding to the 51.8 per cent of the undecomposed monocalcium phosphate.

In this case the determination of the free phosphoric acid and the monocalcium phosphate by titration with uranium acetate are not accurate, and the results are only approximations, as, by boiling the acid liquid (the solution of uranium acetate used having been as usual acidulated), a small part of the pyrophosphate is converted into orthophosphate.

According to theory the phosphoric acid is present in the solution in the following form:—

	Per cent P_2O_5 .	Found. Per cent P_2O_5 .
$CaH_4(PO_4)_2 \cdot H_2O$	28.3	29.20
H_3PO_4	7.0	6.60
$3CaH_2P_2O_7 \cdot 2H_2O$	7.03	6.94
Sum	42.33	42.74

* From the *Zeitschrift Anal. Chemis.*

By the decomposition of half the original monocalcium phosphate during the drying there have been formed :—

	Per cent.	
$\text{Ca}_2\text{P}_2\text{O}_7$	12.60	} Insoluble part.
$\text{Ca}(\text{PO}_3)_2$	9.82	
$\text{CaH}_2\text{P}_2\text{O}_7$	10.71	
H_3PO_4	9.72	
	42.85	} Soluble part.
H_2O	7.15	
	50.00	

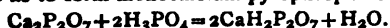
The results above indicated give an interesting explanation of the processes during the desiccation of monocalcium phosphate in a quite new direction. Birnbaum certainly recognised the normal calcium pyrophosphate and free phosphoric acid, but he nowhere mentions having found metaphosphate and monocalcium pyrophosphate. He considers that the decomposition takes place as follows :—



The decomposition cannot take place in this manner, since by the continued action of the temperature monocalcium pyrophosphate is formed from pyrophosphate and free phosphoric acid.

S. Drewsen, who examined the transformations of superphosphates at higher temperatures, does not mention the formation of normal calcium pyrophosphate and metaphosphate. He merely observed that a considerable quantity of monocalcium pyrophosphate is formed even at 100°. But this phenomenon, as I will show below, is occasioned by other factors, and not merely by temperature. He suggests, therefore, that the aqueous solution of superphosphates on analysis should be boiled with nitric acid, as we cannot know if the superphosphate in question has been artificially dried at a high temperature. From the tabular conspectus in which he summarises the results of his experiments, it is seen that the quantity of the phosphoric acid soluble in water remained unaltered even in drying the superphosphates at 300°, for if the aqueous solution of such a dried superphosphate was boiled in nitric acid, the same quantity of phosphoric was found as in the original sample. Drewsen does not, indeed, mention the composition of the superphosphates which he examined, but it is evident from his memoir that he means the soluble phosphoric acid which appears in superphosphates as monocalcium phosphate. He is thus in a serious error, for his results cannot be applied to superphosphates, which contain the soluble phosphoric acid chiefly in the state of monocalcium phosphate.

The author repeated the experiments with superphosphates which contained 18 per cent of soluble phosphoric acid (17 per cent as monocalcium phosphate and 1 per cent as free phosphoric acid), and on drying for four hours at 120°, he observed great losses of soluble phosphoric acid. Slightly different results are reached if free phosphoric acid is found in the superphosphates in addition to monocalcium phosphate. Drewsen's results may be explained on the supposition that he operated upon superphosphates containing at least 80 per cent soluble phosphoric acid in the state of free acid. At high temperatures the free phosphoric acid, or that liberated by decomposition, reacts upon the normal calcium pyrophosphate so as to form monocalcium pyrophosphate :—



The author has proved this reaction. Chemically pure calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7 + 4\text{H}_2\text{O}$) was prepared from calcium chloride and sodium pyrophosphate.

The analysis showed :—

	(Calculated).	
P_2O_5	42.85 per cent.	43.56 per cent.
CaO	34.92 "	34.35 "
H_2O	21.26 "	22.09 "
	99.03 "	100.00 "

A mixture of 2 grms. pyrophosphate and 1.202 grms. phosphoric acid was dried for ten hours in a platinum capsule at 200°. The monocalcium pyrophosphate formed was placed in a litre flask which was filled with water up to the mark. After shaking for an hour, the solution became slightly turbid, and contained free phosphoric acid only in traces. There was found in the solution monocalcium pyrophosphate (without heating with nitric acid) and 4 per cent of phosphoric acid; after the solution had been heated with nitric acid, there were found 56.08 per cent of phosphoric acid by the molybdenum method. In our case there was first formed monocalcium phosphate, which afterwards loses water and passes into monocalcium pyrophosphate.

If we dry monocalcium phosphate at 150° for longer than an hour, we do not find the quantity of free phosphoric acid which corresponds to the monocalcium phosphate taken. This phenomenon led to the thought that the decomposition is different. On examining the aqueous solution, there was found a large quantity of monocalcium pyrophosphate. The author proved by a number of experiments that not merely the temperature reached, but the time during which the desiccation is prolonged at 150°, a higher has great influence on the formation of monocalcium pyrophosphate.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 31ST, 1891.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, *Metropolis Water Act*, 1871.

London, February 7th, 1891.

SIR,—We submit herewith the results of our analyses of the 142 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from January 1st to January 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 142 samples examined, 131 were found to be clear, bright, and well filtered, 1 being recorded as "very slightly turbid," and 10 as "slightly turbid."

As a consequence of the impracticability, during the prolongation of the frost, of obtaining samples of water from some of the standpipes, the record of analytical results included in this Report is more defective than in any that we have hitherto made. Samples of water were occasionally still met with manifesting the evanescent smoky taste spoken of and considered in our previous Report for December; but the analytical results obtained during the first three weeks of the month of January, and recorded in our present Report, continued to be, except for two instances occurring of slight turbidity, entirely

satisfactory. With the breaking up of the long frost, however, a distinct deterioration became noticeable in the character of the water supplied by several of the Thames companies; but only in a single sample, taken on January 30th, was the organic matter present—and that inferred to be of a non-animal origin—at all excessive.

Owing to the almost complete want of samples of the Southwark and Vauxhall Company's water during the early part of the month, the mean results of the examination of this Company's supply recorded in the Tables are, in fact, rather means for the least satisfactory week of the month than for the entire month; whereby they are exposed, in some particulars, to an unduly unfavourable comparison with the mean results recorded in the case of the other Thames companies' supplies.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY'S JUBILEE—1891.

February 24th.

(Continued from p. 105.)

EDWARD FRANKLAND, D.C.L., LL.D., F.R.S.,
President, 1871—1873.

1. *Eudiometer and Calibration Table*.—In this eudiometer ethyl was first analysed.—*Journ. Chem. Soc.*, 1850, p. 263.

(Exhibited by the Science and Art Department, South Kensington).

2. *Isolation of the Organic Radicles, and Conception of their Hydrides as a Class*.—Ethyl butane; ethylic hydride ethane.—*Journ. Chem. Soc.*, 1850, p. 263.

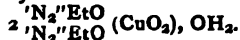
3. *Digester used in the production of organo-metallic compounds, and for chemical reactions under heat and pressure*.—*Journ. Chem. Soc.*, 1850, p. 297.

4. *Organo-metallic Compounds*.—Zinc ethyl, ZnEt_2 ; stannic ethodimethide, SnEt_2Me_2 .

5. *The First Regenerative Gas Burner*.—An intermediate glass (broken) caused the air to pass close to the innermost glass before it reached the flame.—"Ure's Dictionary," vol. ii., p. 562, 1854.

6. *Artificial Human Milk*.—Prepared by the partial removal of casein from, and addition of, milk-sugar to cow's milk.—*Manchester Guardian*, Dec., 1854.

7. *Substitution of 'N₂' for C₂ in Organic Compounds*.—Cupric dinitroethylate—



—*Phil. Trans.*, 1856, p. 59.

8. *Influence of Atmospheric Pressure on the Rate and Light of Combustion*.—The six candles burnt for one hour on the summit of Mont Blanc.—*Journ. Chem. Soc.*, 1861, p. 168.

9. *Organo-boron Compounds*.—Boric ethide, BEt_3 .—*Journ. Chem. Soc.*, 1862, p. 363.

10. *Source of Muscular Power*.—Thompson's apparatus used in the determination of the potential energy in various articles of food.—*Phil. Mag.*, 1866, Series 4, vol. xxii., p. 182.

(Exhibited by the Science and Art Department, South Kensington).

11. *Simple Apparatus for Gas Analysis*.—*Journ. Chem. Soc.*, 1868, p. 109.

12. *Apparatus Used for the Combustion of Hydrogen and Carbonic Oxide under Great Pressure*.—*Proc. Roy. Soc.*, 1868, p. 419.

13. *Thermometric Observations in the Alps*.—Black box

in which water was boiled by the unconcentrated sun's rays at Davos, Dec. 22nd, 1873. The plain thermometer in the box rose to 221° F.—*Proc. Roy. Soc.*, 1874, p. 317.

14. *Self-registering Maximum Solar Thermometer*.—This is essentially a differential air thermometer, one bulb of which is blackened and exposed in vacuo to the solar rays upon a white ground, the other bulb is freely exposed to the air beneath the shade of a white arch. The difference in temperature is read off upon an arbitrary scale attached to the capillary limb of the inverted syphon, the maximum height attained by the mercury in this limb being registered in the usual manner.—*Proc. Roy. Soc.*, 1882, p. 331.

DR. FRANKLAND AND DR. KOLBE.

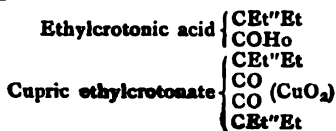
15. *Transformation of Cyanogen (CN) into Oxatyl (COHo)*.—Caproic acid from AyCy .—"Mem. Chem. Soc.," iii., 1847, p. 386.

16. *Polymerisation of Ethylic Cyanide*.—Kyanethine $\text{N}_3(\text{CEt})_3$.—*Journ. Chem. Soc.*, 1848, p. 69.

DR. FRANKLAND AND MR. DUPPA.

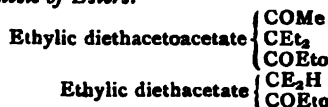
17. *Organo-mercury Compounds*.—Mercuric amyliide, HgAy_2 .—*Journ. Chem. Soc.*, 1863, p. 420.

18. *Transformation of the Acetic into the Acrylic Series of Acids*.—



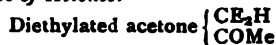
—*Journ. Chem. Soc.*, 1865, p. 133.

19. *Synthesis of Esters*.—



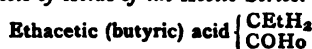
—*Journ. Chem. Soc.*, 1865, p. 395.

20. *Synthesis of Ketones*.—



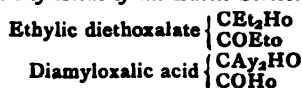
—*Journ. Chem. Soc.*, 1865, p. 401.

21. *Synthesis of Acids of the Acetic Series*.—



obtained by the successive action of sodium and ethylic iodide on ethylic acetate.—*Journ. Chem. Soc.*, 1865, p. 395.

22. *Synthesis of Acids of the Lactic Series*.—



—*Phil. Trans.*, 1866, p. 37.

DR. FRANKLAND AND DR. ARMSTRONG.

23. *Eudiometer for the Determination of Nitrogen in Nitrates and Nitrites*.—*Journ. Chem. Soc.*, 1867, p. 102.

24. *Analysis of Potable Water*.—Tube charged for combustion of water-residue.—*Journ. Chem. Soc.*, 1868, p. 77. (Exhibited by Dr. Frankland).

SIR FREDERICK ABEL, K.C.B., D.C.L., D.Sc., F.R.S.,
President, 1875—1877.

1. Specimen of gun-cotton prepared according to prescription of Schönbein, by F. A. Abel, Aug., 1846, in the Royal College of Chemistry.

2. Specimens illustrating researches on the stability of gun-cotton, 1863—1865.

3. Sample of gun-cotton manufactured by Hall and Son, 1846, buried after explosion at the works, until 1864.

4. Preparations of nitro-glycerin and of gun-cotton (glyoxiline), 1867.

5. Specimens of granulated gun-cotton, 1876.
 6. Specimens of compressed gun-cotton, Abel's system.
 7. Gun-cotton slab fired through from a Martini-Henry rifle, without being exploded.
 8. Gun-cotton slabs perforated by the electric discharge without ignition.
 9. Explosion vessel used in researches on gun-cotton, 1865-1868.
 10. First explosion vessel used in Abel and Noble's researches on fired gunpowder, &c., 1871-1880.
 - Note.*—Largest powder-charge exploded in the vessel, 21 lb.; pressure developed, 43 tons per sq. in.; largest gun-cotton charge exploded, 14 oz. In larger vessels of the same model, 22 lbs. of powder have been exploded, and gun-cotton has been detonated with developments of nearly 70 tons pressure per sq. in.
 11. Vacuum bomb used in researches on the combustion of gunpowder and gun-cotton in rarefied atmospheres, 1867.
 12. Specimens of "cordite," the new smokeless powder.
 13. Photographs showing the 6-in. quick-firing gun, fired with black powder and with cordite (smokeless powder).
- (Exhibited by Sir F. A. Abel).

SIR HENRY ROSCOE, M.P., F.R.S.,
President, 1880-1882.

A complete series of specimens of vanadium compounds:—

Vanadium ore. Roasted ore. Ammonium vanadate. Vanadium pentoxide. Vanadium trisulphide, disulphide, and pentasulphide. Silver hypovanadate. Sodium hypovanadate. Hypovanadic tetrachloride and disulphate. Lead hypovanadate. Aqueous solutions of vanadium dioxide, trioxide, tetroxide, pentoxide, dichloride, trichloride, tetrachloride, and vanadyl trichloride. Divanadyl monochloride. Lead metavanadate. Ammonium metavanadate. Vanadium mononitride, trioxide, pentoxide, silicon alloy, and platinum alloy. Vanadous sulphate. Vanadium oxidibromide and trichloride. Vanadyl trichloride. Vanadium tetrachloride (decomposed) and dichloride. Potassium anhydrovanadate and anhydrochromate. Vanadium metal, pentoxide, and nitride. Barium hypovanadate. Vanadic vanadate. Ammonium magnesium phosphate (from Berzelius's vanadium). Metavanadic acid. Sodium anhydrovanadate. Ammonium hypovanadate. Hypovanadic hydrate. Thallium tetravanadate, deca- and hexa-kaivanadate. Silver octa-kaivanadate. Metavanadic acid. Ammonium vanadate and vanadite. Vanadium sesquioxide. Artificial vanadinite. Ammonium metavanadate. Sodium orthovanadate. Silver orthovanadate. Sodium orthovanadate (fused mass) and pyrovanadate. Pyrovanadate of lead. Sodium octavanadate. Barium pyrovanadate. Silver pyrovanadate. Vanadyl dichloride. Calcium divanadate. Sodium vanadate-vanadite.

(Exhibited by Sir H. E. Roscoe).

J. H. GILBERT, LL.D., F.R.S.,
President 1882-1883.

Dr. Gilbert, having been engaged with Sir J. B. Lawes in the conduct of the Rothamsted Investigations from 1843 up to the present time, sends the following illustrations of some of the lines of inquiry undertaken:—

Apparatus used in an investigation by Messrs. Lawes, Gilbert, and Pugh, in the years 1857, 1858, 1859, and 1860, to determine whether plants assimilate free or uncombined nitrogen. The plants were grown in ignited pomice or soil (with plant-ash added), either with no other supply of combined nitrogen than that contained in the seed sown, or with the addition of known and limited quantities of combined nitrogen; and they were supplied with washed air, and washed carbonic acid. The conditions of growth were, therefore, those of sterilisation; and there was, under such conditions, no gain from free

nitrogen, in the growth of either Gramineæ, Leguminosæ, or other plants.

Plate of Gramineous plants grown in 1857 and 1858; and coloured photograph, of coloured scale-drawings, of Leguminous plants grown in 1860.

Three enlarged Photographs, of Leguminous Plants grown in Experiments in 1889, on the Question of the Fixation of Free Nitrogen; in some cases with sterilisation, and in others with microbe-seeding of the soil. With suitable microbe infection of the soil there was abundant formation of the so-called "Leguminous nodules" on the roots of the plants; and there was, coincidentally, very considerable fixation of free nitrogen. The evidence at present at command points to the conclusion that the free nitrogen is fixed in the course of the development of the organisms within the nodules, and that the resulting nitrogenous compounds are absorbed and utilised by the higher plant.

Coloured Drawing, by Lady Lawes, of the Rothamsted Rain-gauges. For the purpose of accurate measurement of the rain, and of obtaining sufficient quantities for analysis, a large gauge of one-thousandth of an acre area has been in use since the beginning of 1853; also an ordinary funnel-gauge of 5 inches diameter; and these are represented in the drawing. An 8-inch "Board of Trade" copper-gauge has also been in use since January, 1881. The funnel portion of the large gauge is constructed of wood lined with lead; the upper edge consisting of a vertical rim of plate glass, bevelled outwards. The rain is conducted by a tube into a galvanised iron cylinder underneath, and when this is full it overflows into a second cylinder, and so on into a third and fourth, and finally into an iron tank. Each of the four cylinders holds rain corresponding to half an inch of depth, and the tank an amount equal to 2 inches. Each cylinder has a gauge-tube attached, graduated to read to 0.002 inch, but which can be read to 0.001 inch. Small quantities are transferred to a smaller cylinder with a gauge-tube graduated to 0.001, or one-thousandth of an inch.

Coloured Drawing, by Lady Lawes, of the Rothamsted Drain-gauges. The three "drain-gauges," each of one-thousandth of an acre area, for the determination of the quantity and composition of the water percolating respectively through 20 inches, 40 inches, and 60 inches depth of soil (with the subsoil in its natural state of consolidation), have been in use since September, 1870,—that is, for a period of more than twenty years. The gauges were constructed by digging a deep trench along the front, gradually undermining at the depth required, and putting in plates of cast-iron (with perforated holes), to support the mass. The iron plates were then kept in place by iron girders, and the ends of the plates and of the girders supported by brickwork on three sides. Trenches were then dug bit by bit round the block of soil, which was then enclosed on each side by walls of brick laid in cement. Below the perforated iron bottom a zinc funnel, of the same area as the soil, was finally fixed, and the drainage water is collected and measured in galvanised iron cylinders, with gauge-tubes, as in the case of the rain.

Photograph of a case (now in the Science Museum, South Kensington), illustrating the influence of different manures on the botanical composition of the Mixed Herbage of Permanent Grass-land.

A set of bound volumes of Rothamsted Memoirs, &c., published 1847 to 1890, inclusive. Also the annual "Memoranda" for 1890.

Book of Drawings and Plans of the "Lawes Testimonial Laboratory," Rothamsted, Herts.

(Exhibited by Sir J. B. Lawes and Dr. Gilbert.)

W. H. PERKIN, Ph.D., F.R.S.,
President, 1883-1885.

Dinaphthylguanidine.
Bromacetic acid. Dibromacetic acid. Dibromacetamide.

Glyoxylic acid (cryst. $C_2H_4O_4$). Calcium glyoxylate. Diethyl tartrate. Diethyl diacetotartrate. Diethyl benzoyltartrate. Diacetarceic anhydride. Diethyl diacetarceamate.

Dibromosuccinic acid.

Tartaric acid (inactive, from argentic dibromosuccinate). α Azoamidonaphthalene.

Mauveine. — The base of the mauve dye; the first of the coal-tar colours; discovered in 1856.

Mauveine hydrochloride. Mauveine hydriodide. Mauveine sulphate. Mauveine acetate. Mauveine carbonate. Nitrate of parasafranine (prepared from Mauveine).

Salicyl aldehyde (salicyl). Salicylaldehyde and acetic anhydride.

Coumarin (from Tonka bean). Coumarin (artificially prepared). Propionic coumarin. Butyric coumarin. Valeric coumarin. Chlorocoumarin. Tetrachlorocoumarin. Bromocoumarin. α Dibromocoumarin. β Dibromocoumarin. Coumarilic acid. Potassium coumarilate. Baric sulphocoumarilate. Bromopropionic coumarin.

Anthracene. Anthraquinone. α Dibromanthraquinone. β Dibromanthraquinone. Barium disulphoanthraquinonate. Monochloranthracene. Dichloranthracene. Monobromanthracene. Dibromanthracene. Dichloranthracene and Picric acid. Sodium disulphodichloranthracenate. Strontium disulphodichloranthracenate. Barium disulphodichloranthracenate.

Anthraflavic acid. Diacetylanthraflavic acid. Barium anthraflavate.

Isoanthraflavic acid. Anthrapurpurine (sublimed). Triacetylanthrapurpurine.

Alizarine (sublimed). Acetylalzarine. Diacetylalzarine. Bromalzarine. α Nitroalzarine. α Amidoalzarine.

Phenylacrylic acid (cinnamic acid). Phenylacrylic-crotonic acid. Phenylacrylicangelic acid.

Cumenylacrylic acid. Cumenylacryliccrotonic acid. Cumenylacrylicangelic acid. Sodium cumenylcrotonate.

Methylparoxyphenylacrylic acid. Methylparoxyphenylacrylate of methyl. Methylparoxyphenylcrotonic acid. α Methylorthoxyphenylacrylic acid. β Methylorthoxyphenylacrylic acid. β Methylorthoxyphenylcrotonic acid. β Methylorthoxyphenylangelic acid. Barium β Methylorthoxyphenylacrylate.

Cinnamonylacrylic acid. Cinnamonylcrotonic acid. Isobutenylbenzene. Isobutenylbenzene dibromide. Isopropylallylbenzene. Isobutenylvinylbenzene (Iso butenyl cinnamene).

Parallylanisoll (anisoll, made artificially). Orthoallylanisoll. Butenylanisoll. Iso butenylanisoll.

Vinylbenzene (cinnamene), polymerised. Vinyl-p-anisoll, polymerised. Vinyl-o-anisoll, polymerised. Vinyl-isopropylbenzene, polymerised.

Orthoisobutenylphenol.

Acetomalic anhydride. Maleic anhydride (obtained by distillation of the above).

Chlorofumaric acid. Amidofumaramide. Potassium chloromaleate. Ethyl chloromaleamate.

Diphenyleneketone oxide.

Nitrophenyldiazobenzeneacetoneitrile. Nitrophenyldiazotolueneitrile.

Tritylenetriamine. Tolytriparalolylenetriamine.

Butyrylphenol. Propionylphenol.

(Exhibited by Dr. Perkin.)

Dr. HUGO MÜLLER, F.R.S.,
President, 1885-1887.

WARREN DE LA RUE and HUGO MÜLLER.

Emodin. Chrysophan. Original Resin of *Ficus rubiginosa*, in which the Sycocerylic acetate was discovered. Sycocerylic acetate. Sycocerylic alcohol.

HUGO MÜLLER.

Chlorinated Derivatives obtained by the Iodine process:—

Dichlorobenzene. Quatrichlorobenzene. Hexichlorobenzene. Malonic acid, from Cyanoacetic acid. Methyl-

Pyrocatechin, or Guaiacol, from Wood Kreasot. Methyl-Homo-Pyrocatechin, from Wood Kreasot. Homo-Pyrocatechin. Inosite, from Cochineal. Guanine Hydrochlorate, from Cochineal. Quercite, from the leaves of *Chamaecrops humilis*. Cocosite, a substance resembling Inosite, from the leaves of several species of Coconut Palm.

(Exhibited by Dr. Hugo Müller.)

(To be continued.)

CHEMICAL SECTION OF THE FRANKLIN INSTITUTE.

Held at the Institute, Tuesday, January 20, 1891.

Dr. WM. H. WAHL, President, in the chair.

THE annual report of the Treasurer was read and approved.

The report of Mr. H. Pemberton, Jun., as chairman of the committee of conference of the Chemical Section, appointed to confer with a similar committee of the American Chemical Society, was read and accepted. This committee was appointed by the President a few days after the last meeting of the section in December, and in response to a request for such a committee from Mr. A. A. Breneman, chairman of the committee of arrangements of the American Chemical Society.

The object of this conference was to consider, in a preliminary way, the question of forming a general organisation of American chemists, who should thus constitute a national society. A general meeting of eighteen delegates, representing seven different chemical organisations, was held in connection with the general meeting of the American Chemical Society at the University of Pennsylvania, on the 30th of December. On the following day a meeting of the chairmen of the various committees of conference was held at the Manufacturers' Club, in Philadelphia, and, as a result of the two meetings, a set of resolutions was adopted, a copy of which was submitted by Mr. Pemberton as a part of his report to the section.

Inasmuch as another meeting of the various conference committees is provided for in the above-mentioned resolutions, the committee was continued for the performance of such duties as were implied in the resolutions. After Mr. Pemberton's report had been accepted, the President extended the thanks of the section to the committee for its action.

Mr. LEE K. FRANKEL then read a paper "On the Electrolysis of the Metallic Sulpho-cyanides."

Prof. Geo. A. KOENIG followed with a paper, entitled "Is Sulphuric Hydrate Volatile at Ordinary Temperatures?"

Prof. Koenig's observations and experiments tended towards an affirmative answer of the question which formed the title of his paper, and some interesting discussion was evoked.

Dr. TUTTLE referred to recorded experiments, in which the absence of change in solutions of barium salts exposed to the possible evaporation of sulphuric acid tended to prove the non-volatility of the acid.

Prof. SMITH cited some observations made by himself in connection with electrically deposited mercury, in which a weight of 0.3 gm. of that metal lost in the course of something less than twenty-four hours a weight of 0.002 gm., presumably by evaporation.

The paper by Dr. HANS V. STROMBECK "On the Specific Heat of Brines of Different Specific Gravity, and on the Determination of the Specific Heat of a Body Generally," was read by title.

A paper from Mr. J. M. EMANUEL, U.S.N., "On the Occurrence of Amberite, Ambrite, or Fossil Gum, in a Coal Seam at Hawakawa Colliery, Bay of Islands, N.Z.," was read by the Secretary.

Prof. SMITH then presented a paper "On the Electrolytic Separation of Certain Metals in Phosphate Solutions."

After a number of interesting comments upon Prof. Smith's contribution, the section adjourned.

NOTICES OF BOOKS.

On the Greening of French Vegetables with Sulphate of Copper. Report by Sub-Committee of the Glasgow Corporation.

THE industry of preserving fruits and vegetables has, unfortunately, its chief seat in France. "Unfortunately" we are justified in saying, on the faith of Professor Gautier's admission, that "nine-tenths at least of the green preserved vegetables sold in France or abroad are re-greened with sulphate of copper." This salt is added, it seems, in the proportion of 8 to 27 parts per 100,000 of vegetables.

This practice has sprung up in obedience to a mistaken demand on the part of the consumer. The idea of colour is one essentially foreign to the kitchen and the dining-room, where flavour, aroma, and wholesomeness should alone be taken into consideration. This fraudulent addition of copper sulphate is illegal in France, but breaches of the law are winked at.

It is, indeed, urged that no injury to the health of consumers—who are many—has hitherto been detected. But this assertion merely means that no acute and fatal cases have occurred. Knowing that the salts of copper are poisons we are slow to believe that their habitual introduction into the human system, even if in small proportion, can be harmless. One of the French experts who have examined the question (M. Bussy) thinks that the risk to public health should not be run. He asks with what consistency can a Government which interdicts the use of poisonous pigments in the manufacture of children's toys sanction, tacitly at least, the colouring of articles of food with salts of copper.

M. Pasteur very wisely suggests that all peas or other vegetables re-greened with sulphate of copper shall be labelled as containing this salt, at the peril of the maker and the seller.

It has even been recommended that re-greening for exportation should be permitted, *but not for home use!* We find further that cupriferous peas are actually known in the trade as "*petits pois à l'anglaise*."

We can only recommend that until the Customs are authorised to seize and destroy all coppered vegetable, the local authorities should not be slack in prosecuting the vendors of re-greened vegetables.

Why does not a trade in honest preserved vegetables spring up in Canada, the West Indies, &c.? From every point of view such an attempt should be made and encouraged.

A Series of Chemical Problems, with Key, for Use in Colleges and Schools. By T. E. THORPE, B.Sc., Ph.D., F.R.S. Revised and enlarged by W. TATE, Assoc.-N.S.S., F.C.S.; with a Preface by Sir H. E. Roscoe, B.A., Ph.D., F.R.S. New edition. London: Macmillan and Co.

THE recommendation of this work expressed by Sir H. E. Roscoe in his preface to its first edition in 1870 may still be accepted as well founded. The calculations are exceedingly well chosen, and the solution of the questions necessitates an accurate knowledge of the theoretical phase of chemistry. It is, of course, possible that a student might have a perfect mastery of such calculations, and yet be utterly helpless in the laboratory. But if this work is used in conjunction with sound practical training it will prove invaluable.

CORRESPONDENCE.

EXPLOSION—A WARNING!

To the Editor of the Chemical News.

SIR,—A few drops of strong sulphuric acid were added to a few crystals of potassium permanganate in a clean test-tube kept cool with water, and the production of ozone having been demonstrated, the test-tube containing the mixture was placed in a test-tube stand. Some *ten minutes* afterwards the mixture exploded with great violence, shattering bottles, flasks, &c., and scattering the contents of the tube in all directions. I can find no warning in any text-book as to danger in performing this common experiment, nor have I ever had an explosion with it before. It may prevent a serious accident if I send this note of warning to you for publication.—I am, &c.,

D. B.

P.S.—I know that manganese heptoxide is formed, and that it explodes when heated or in contact with organic matter, but this was *in the cold*, and no organic matter was present to my knowledge.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxii., No. 5, February 2, 1891.

The Photography of Colours.—G. Lippmann.—(See p. 87).

On the Basicity of the Organic Acids, according to their Conductivity. Mono-basic and Bi-basic Acids.—Daniel Berthelot.—The author proposes to characterise the basicity of the organic acids by means of the electric conductivity of mixtures of these acids with potassa made in different proportions. The existence of acid salts in the solutions forms the knot of the problem, and the novelty of his researches consists in the definition by this means of the peculiar characters of the organic acids.

On the Reaction of the Oxyalkyl Derivatives of Dimethylaniline.—Ed. Grimaux.—It appears not merely that the introduction of an OR group into dimethylaniline modifies its reactional aptitudes and affects the nature of the colour formed, but that there is a great difference in the behaviour of the oxyalkylised dimethylanilines according as the group OR occupies an ortho- or a meta-position with respect to the group N(CH₃)₂.

On Levosine—A New Proximate Principle of the Cereals.—C. Tanret.—The composition of levosine dried at 110° may be represented by the formulæ C₄₈H₄₀O₄₀ or (C₁₂H₁₀O₁₀)₄. It yields on analysis the same figures as starch and dextrine, and on the application of Raoult's method its molecular weight is found to be 652. The anhydrous product on exposure to the air resumes 11 per cent of its weight of water, which gives for hydrated levosine (C₁₂H₁₀O₁₀H₂O)₄. Levosine is a white body, amorphous and almost tasteless. It dissolves in water in all proportions, and is readily soluble in weak alcohol, but scarcely in alcohol at 95°. It softens at 145°, but does not melt decidedly until 160°. Its specific gravity is 1.62. It is lævo rotatory:—[α_D] = -36°.

On the Enrichment of the Blood in Hæmoglobine according to the Conditions of Existence.—A. Müntz.—From comparative analysis of the blood of rabbits living on the Pic du Midi, and of those living in

the plains, it is found that when animals live at a great altitude, that is in a medium where the tension of the oxygen is notably diminished, their blood becomes richer in hæmoglobine, as is shown by the increase of fixed matter, and especially in iron. It thus acquires a greater absorbent power for oxygen, which compensates the effect of the rarefaction of the air. A sojourn of seven years, comprising many generations of rabbits, has therefore sufficed to effect this enrichment of the blood.

The Influence of the Nature of Soils upon Vegetation.—G. Raulin.—A mixture of four soils, sand, clay, lime-stone, and peat-earth, yielded both beets and maize of a weight superior to that of plants grown in any of the earths separately; the beets were also richer in sugar than the average. The results did not by any means follow in the same order; for the weight of the crop of maize clay took the first rank among the unmixed soils, and the sand was decidedly inferior. For the weight of beets, peat took the first rank and sand the lowest. For richness in sugar, clay gave the lowest yield and lime-stone the maximum. All the soils had received no manure for several years, and were very much exhausted.

No. 6, February 9, 1891.

On the Experiment of M. Wiener.—H. Poincaré.—A purely mathematical paper.

On the Communication of M. Poincaré.—M. Berthelot.—The author holds that to his knowledge there does not exist any purely chemical reaction which can, strictly speaking, furnish a measure of luminous energy. It is not necessary to ascribe to the luminous radiations any appreciable expenditure of energy in effecting the chemical phenomena of photography.

Photographic Reproduction of the Solar Spectrum in its Own Colours.—Edmond Becquerel exhibited proofs which he had obtained more than forty years ago, and which have remained unchanged, though they have been on several occasions examined and studied by daylight.

On the Conductivity of Tri-basic Organic Acids—A New Characteristic of Basicity.—Daniel Berthelot.—Electric conductivities yield a new characteristic for the basicity of acids whose atomic weight is known. We may thus determine by purely physical procedures the equivalent and the basicity of an acid, though knowing neither its formula nor even its elementary composition.

The Combinations formed by Ammonia with the Chlorides.—M. Joannis.—Contrary to the opinion of Rose, this author has obtained a compound of sodium chloride of the composition $\text{NaCl} \cdot 5\text{NH}_3$. He has not succeeded in forming the corresponding potassium compound, but he has obtained $\text{BaCl}_2 \cdot 4\text{NH}_3$.

On the Formation of the Isopurpurates.—Raoult Varot.—Silver, mercury, and copper cyanides do not react upon picric acid or the picrates so as to form isopurpurates. Zinc cyanide, on the contrary, reacts, but more slowly than the alkaline cyanides.

On the Manner of Combination of Sulphuric Acid in "Plastered" Wines, and on the Detection of Free Sulphuric Acid.—L. Magnier de la Source.—Wines containing, respectively, 4 and 18 grms. per litre of free sulphuric acid cannot be drunk; with 1 grm. per litre the wine is very acid but good, and with 0.55 grm. it is very agreeable. Below 1 grm. per litre the addition of sulphuric acid cannot be detected by an analysis of the ash.

Moniteur Scientifique, Quasneville.
Series 4, Vol. iv., Part 2.

Manufacture and Composition of Peat Litter.—P. Kulisch (*Chemiker Zeitung*).—Analyses of peat used as litter in cow-houses, &c.

Assay of Essential Oils by Maumené's Reaction.—Rowland Williams.—From the CHEMICAL NEWS.

Formation of Chloroform.—E. Koefoed.—In the action of a solution of chloride of lime upon alcohol there are formed for 3 mols. hypochlorite, 1 mol. chloroform, 1 mol. calcium carbonate, and $\frac{1}{2}$ mol. calcium hydrate. Hence, Liebig's formula for the production of chloroform is not correct.

Absorption of Iodine by Essential Oils.—From the CHEMICAL NEWS.

Mandragorine.—F. B. Ahrens (*Chemiker Zeitung*).—The author obtains from the root of this plant a base— $\text{C}_{17}\text{H}_{23}\text{NO}_3$ —an isomer of atropine.

Presence of Oxygenated Water in Ether.—Brunner (*Pharm. Zeitung*).

Explosive Compounds Contained in Ether.—J. König (*Land. Vers.*).—On submitting to fractionated distillation the residue left on rectifying commercial ether, white fumes were given off at about 100°, and a violent explosion took place. This result is due to the presence of hydrogen peroxide.

Musk: Natural and Artificial.—These two compounds are not absolutely identical. Quinine sulphate completely removes the odour of artificial musks, whilst natural musk undergoes no change. The artificial musk also undergoes changes on keeping.

Revue Universelle des Mines et de la Metallurgie.
Vol. xii., No. 3.

This issue does not contain any chemical papers.

MISCELLANEOUS.

The Proposed Benevolent Fund.—We have much pleasure in announcing that Mr. Ludwig Mond has given £500, and Dr. J. H. Gladstone £100 to this fund.

Announcement.—Mr. Albert Fuerst, of the firm of Fuerst Bros., chemical merchants, 17, Philpot Lane, London, E.C., left for New York on Wednesday, the 25th ult., by s.s. *Majestic*, to manage the American branch office of the firm.

Royal Institution.—Professor Victor Horsley, F.R.S., will give a discourse on "Hydrophobia" on Friday, March 20th, in place of Professor W. E. Ayrton, F.R.S., who is unable to give his promised lecture on "Electric Meters, Motors, and Money Matters."

MEETINGS FOR THE WEEK.

- MONDAY, 9th.—Medical, 8.30.
— Society of Arts, 8. "Photographic Chemistry," by Prof. R. Meldola, F.R.S.
- TUESDAY, 10th.—Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8.
— Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley, F.R.S.
- Society of Arts, 8. "Enamelling and Damascening," by J. Starkie Gardner.
- WEDNESDAY, 11th.—Society of Arts, 8. "Electricity in Relation to the Human Body," by H. Newman Lawrence and Arthur Harries, M.D.
— Geological, 8.
— Pharmaceutical, 8.
- THURSDAY, 12th.—Royal, 4.30.
— Mathematical, 8.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "Modern Chemistry in Relation to Sanitation," by Professor C. Meymoit Tidy.
- FRIDAY, 13th.—Royal Institution, 9. "The Culture of the Singing Voice," by Felix Semon.
— Society of Arts, 4.30. "The Science of Colour," by Captain Abney.
— Astronomical, 8.
- SATURDAY, 14th.—Royal Institution, 3. "The Forces of Cohesion," by The Right Hon. Lord Rayleigh, F.R.S.

THE CHEMICAL NEWS.

VOL. LXIII., No. 1633.

ON THE SYNTHESIS OF PROTEIC SUBSTANCES.

By P. SCHÜTZEN.

THE synthesis of nitrogenous substances, so-called proteic, entering into the constitution of the tissues and the liquids of the living organism, is a problem so complex that we cannot hope to find its complete solution by a single effort, however suitably directed.

The results of the experiments which the author submits seem to him calculated to lead to the object, and to furnish a good clue to the way to be followed. From this point of view they merit notice.

In an extended series of researches which have formed the subject-matter of several memoirs presented to the Academy, the author has made known the terms resulting from the decomposition of the proteic matters, albumenoids, or others, by hydration, under the influence of bases (baryta). For the better understanding of what is to follow, the author recapitulates and sums up the most important results of his researches.

1. Proteic matter, when it is hydrated in presence of baryta at a temperature higher than 100° , utilises approximately as many molecules of water (H_2O) as it contains atoms of nitrogen.

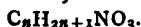
2. A fraction of the total nitrogen, varying with the nature of the substance employed from $\frac{1}{2}$ to $\frac{1}{3}$, is separated out in the form of ammonia. There is observed at the same time the liberation of oxalic and carbonic acids in such proportion that for 2 molecules $2NH_3$ of free ammonia we find 1 molecule of free bibasic acid (CO_2 and $C_2H_2O_4$).

3. The other terms of the decomposition are all amido-compounds. The elementary composition of their mixture answers exactly to an expression of the form



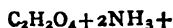
with a slight excess of oxygen.

4. This mixture is formed of two series of terms: the one, of the form $C_nH_{2n-1}NO_2$ ($n=2, 3, 4, 5, 6$), are amido-derivatives of the fatty acids $C_nH_{2n}O_2$, which may be obtained synthetically by the action of the chlorine derivatives of the fatty acids upon ammonia. The others of the form $C_nH_{2n-1}NO_2$ ($n=4, 5$) may be regarded as anhydrides of the amido-oxyacids—

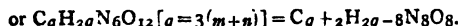
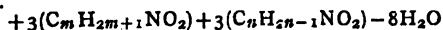


The author has some years ago realised the synthesis of compounds of the form $C_nH_{2n-1}NO_2$ (leucines), presenting the same characters as those obtained by the hydration of the proteic substances by the action of the ethylenic bromides upon the zinc compounds of the fatty amido-acids $C_nH_{2n-1}NO_2$.

A proteic substance such as albumen may be regarded in broad outline as formed of—



Oxalic acid.



If we put $q=28$, the foregoing formula leads to numbers which approach closely to those obtained by the elementary analysis of albumen. It is distinctly understood that there is here no question of a molecular formula.

After this study of an analytical order, which the author believes he has pushed as far as possible, the inverse

problem presents itself. Can we, with the elimination of water, re-combine the above amides and amido-compounds of a relatively simple constitution so as to form complex bodies approaching to the proteic matters by their constitution and the totality of their chemical characters? In other words, can we effect the synthesis of a proteic substance by setting out from the simple products of its decomposition by hydration?

As numerous attempts made in this direction remained fruitless, the author was led to fear that on the decomposition by hydration under the influence of baryta, there may be produced inter-molecular transpositions of the kind which saccharose undergoes when it is split up into lactic acid. If it were thus, the process of the synthesis of the proteic-matters would be much less simple, and in place of consisting merely of the reunion of several molecules with the elimination of water (as it happens in the formation of the compound ethers and the neutral fatty matters), it might be complicated by a molecular transposition inverse of that produced by the alkalies—a transposition which chemists are not yet able to realise at their will.

The author's recent experiments tend to remove this cause of complication. He has, in fact, succeeded in forming a nitrogenous compound, which, from its characters, should rank in the class of the proteic compounds. It has been obtained by eliminating water, and combining the ultimate and crystallisable products derived from the decomposition of albumen and fibrine under the influence of baryta.

The mixture of amido-compounds ($C_mH_{2m+1}NO_2$ and $C_nH_{2n-1}NO_2$), along with about 10 per cent of urea, finely ground and dried at 110° , was intimately mixed with $1\frac{1}{2}$ parts by weight of phosphoric anhydride. The whole was heated in a flask in the oil bath.

Below 120° no change was produced, and the mass remains in a state of powder. About 125° the dehydrating action begins and terminates in a few instants. The phosphoric anhydride is rapidly hydrated at the expense of the water, the elements of which are drawn from the amido-compounds. The mass becomes pasty, and solidifies into a compact compound without turning appreciably brown.

After cooling it is dissolved in a small quantity of water and several volumes of alcohol are added to the solution. We obtain thus a copious precipitate which is washed in alcohol and re-dissolved in water. The solution is filtered to eliminate a little insoluble matter. It is then freed from phosphoric acid by means of a slight excess of baryta—an excess which is separated by precipitation with an equivalent dose of sulphuric acid. The liquid is filtered again and concentrated in the water-bath, giving an amorphous product soluble in water, and precipitable by alcohol in white curdy clots.

The substance thus obtained presents great analogies to the characters of the peptones. Its aqueous solutions are precipitated by tannin, picric acid, mercuric chloride, acid mercuric nitrate, Millon's reagent, potassium diiodide and iodo-mercurate and phosphotungstic acid in presence of hydrochloric acid, phosphomolybdic acid, lead acetate and sub-acetate. It is not precipitated, at least in the cold, by potassium cyanide in presence of acetic acid.

If mixed with caustic potassa and some drops of solution of copper sulphate, it takes a rose-red colouration. This synthetic pseudo-peptone, if heated with nitric acid, after evaporating off the excess of acid, gives a yellow residue which turns orange with ammonia, and which, if heated, is abruptly decomposed with production of a swollen mass of carbon as it happens with gelatin.

If heated upon a sheet of platinum it is carbonised and tumefied, giving off the characteristic odour of burnt animal matter.

It will be interesting to submit to this reaction, one by one, the various amido-derivatives of the proteine compounds, so as to determine which of them play an indis-

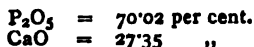
pensable and preponderating part in the formation of the proteine molecules.—*Comptes Rendus*, Vol. cxii., No. 4, p. 198.

DETERMINATION OF WATER IN SUPERPHOSPHATES.*

By JULIUS STOKLASA.

(Concluded from p. 115).

THE mono-calcium phosphate dried at 205° was treated with water. The solution contained traces of free phosphoric acid, and a considerable quantity of mono-calcium pyrophosphate. When the watery solution had been boiled with nitric acid there were found 16·2 per cent of phosphoric acid, but only 2·3 per cent before boiling. The calcium meta-phosphate eliminated had the following composition:—



If dried at 210° it lost 21·5 per cent of water. The residual vitreous calcium meta-phosphate is not soluble in water; in the aqueous solution there were found 0·86 per cent soluble phosphoric acid.

The finely pulverised meta phosphate was thoroughly washed and dissolved in *aqua regia* or undiluted sulphuric acid. The analysis gave:—



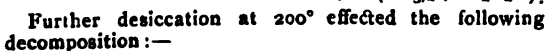
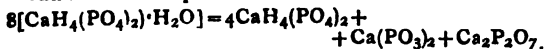
The chemical process is in this case very simple; the mono-calcium pyrophosphate loses 1 mol. of water and becomes metaphosphate, $\text{CaH}_2\text{P}_2\text{O}_7 = \text{Ca}(\text{PO}_3)_2 + \text{H}_2\text{O}$.

The vitreous metaphosphate formed adheres so firmly to the sides of the glass or platinum capsules that it is difficult to determine the remaining matter soluble in water.

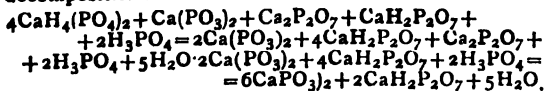
In all the experiments above mentioned it is necessary to spread out the mono-calcium phosphate uniformly in the capsule in order to obtain concordant results as in this manner the temperature acts uniformly upon the mono-calcium phosphate. The results obtained by drying the mono-calcium phosphate at different temperatures are given in the form of a table. The percentage of mono-calcium phosphate decomposed by exposure for an hour to different temperatures varies from 1·84 at 105° to 48·20 at 200°. These results do not agree with the experiments of Birnbaum and Drewson.

The chemical process on the desiccation of mono-calcium phosphate may thus be represented:—

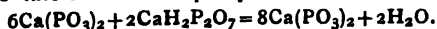
Influence of temperature at 200° for one hour—



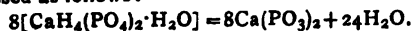
Further desiccation at 200° effected the following decomposition:—



Finally, if the pyrophosphate is completely decomposed at 210° into calcium metaphosphate and water:—



All these transformations, on drying at 210°, may be expressed as follows:—



On Normal Butylamines.—A. Berg.—The author obtains these substances by causing ammonia in a hydro-alcoholic solution to act upon normal butyl chloride.—*Comptes Rendus*, Vol. cxii., No. 8.

* From the *Zeitschrift Anal. Chemis.*

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

February 19th, 1891.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Walter Johnson Cooper, High Street, Mitcheldean, Gloucester; Charles F. Forshaw, LL.D., D.Sc., Bradford, Yorks; John Alfred Foster, Royal Naval College, Greenwich; Claude Hooper Bater, 4, Westbank Terrace, Gibson Street, Hillhead, Glasgow; William L. Hiepe, Ph.D., 21, Acomb Street, Manchester; F. Stanley Kipping, Ph.D., D.Sc., 7, Milborne Grove, South Kensington; Charles Ainsworth Mitchell, 27, Farnley Road, South Norwood; Percy Morrice Randall, 3, Belsize Park Gardens.

Messrs. Holland Crompton, R. H. Davies, and Bernard Dyer were appointed by the meeting to audit the Treasurer's accounts.

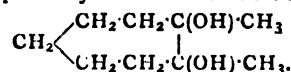
The following were duly elected Fellows of the Society.—Messrs. John Charles Aydans; Henry Austin Appleton; Charles Norrish Adams, M.A.; John Frederick Bloomer; Clayton Beadle; Robert John Brown; Thomas Byrne; Arthur Cole, B.A.; Arthur Colesfax, B.A., Ph.D.; Charles Henry Corbett; Hendrie Thomas Donovan; Robert Bond Greaves; Ernest F. Hooper; Frederick William Harrold; Moses William Jones; Henry Charles Jenkins; Frederick Herbert Moore; Reginald Tom Marshall; Edgar J. Millard; William Morley Martin; Arnold Whitaker Oxford; Michael Samuel Pickering; William Jackson Pope; Tom Kirke Rose; R. Stockdale; Matthew Carrington Sykes; Herbert D. Shaw; R. Greig Smith; Kenelm Edward Symes; Howard C. Sucré; A. H. Tapp; Frederick William De Velling, B.A.; David Wilkinson; Thomas M. Wyatt; Stephen Newcombe Wellington; Dr. W. Will.

The following papers were read:—

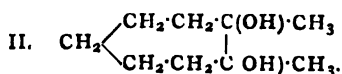
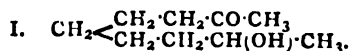
9. "The Action of Reducing Agents on *aa'*-diacetylpentane. Synthesis of dimethyldihydroxyheptamethylene." By F. STANLEY KIPPING, Ph.D., D.Sc., and W. H. PERKIN, Jun., Ph.D., F.R.S.

On reducing *aa'*-diacetylpentane $\text{COMe} \cdot [\text{CH}_2]_5 \cdot \text{COMe}$ (*Trans. Chem. Soc.*, vol. lvi., 330), dissolved in moist ether, with sodium, it is converted into a colourless liquid of the composition $\text{C}_9\text{H}_{18}\text{O}_2$. The method of preparation, properties, and some derivatives of this reduction product are described in the paper, and also various experiments made with the object of determining its constitution.

The author's investigations have shown that the reduction product must be regarded as a dimethyldihydroxyheptamethylene of the constitution



This conclusion is based on the following considerations:—The reduction product is formed by the addition of two atoms of hydrogen to diacetylpentane, and may, therefore, theoretically have the constitution represented by one of the following formulæ:—



As in the one case the compound would be an open-chain ketone alcohol (formula I), and in the other a dihydroxy-derivative of a closed carbon chain (formula II), it is comparatively easy to ascertain which of the two

formula represents the constitution of the compound. 1. The reduction product does not combine with hydroxylamine, or with phenylhydrazine. 2. It yields a diacetyl derivative of the composition $C_{13}H_{22}O_4$ with acetic anhydride. 3. Phosphorus pentabromide converts it into a dibromide of the composition $C_9H_{16}Br_2$. 4. It is not acted on by such reducing agents as zinc and chlorhydric acid, sodium amalgam, or sodium and alcohol. 5. On reduction with hydrogen iodide, it is converted into a hydrocarbon of the composition C_9H_{18} .

These facts, the authors think, are sufficient to warrant the conclusion that the reduction product is a dimethyldihydroxyheptamethylene of the constitution given above.

Dimethyldihydroxyheptamethylene, $C_9H_{18}O_2$, is a thick, colourless liquid, boiling at 201° (180 m.m.); it is only sparingly soluble in cold water, but miscible with alcohol, ether, &c., in all proportions. The sodium derivative, $C_9H_{17}O_2Na + H_2O$, is a colourless, semi-crystalline, very deliquescent compound.

Dimethyldibromoheptamethylene, $C_9H_{16}Br_2$, prepared by treating the dihydroxy-compound with phosphorus pentabromide in chloroform solution, is a thick, colourless oil.

Dimethylhydroxyiodoheptamethylene, $C_{10}H_{17}OI$, is formed when the glycol is heated with hydrogen iodide; it is a colourless liquid, with a pleasant, sweetish smell.

Dimethylheptamethylene diacetate, $C_9H_{16}(OAc)_2$, is obtained when the dihydroxy-compound is boiled with acetic anhydride; it boils at $199-202^\circ$ (65 m.m.) and is readily hydrolysed by dilute soda.

Dimethylheptamethylene, C_9H_{18} , is obtained in the form of a colourless, mobile oil, when dimethyldihydroxyheptamethylene is heated with hydriodic acid and amorphous phosphorus; it boils at $153-154^\circ$ and has an odour very like that of light petroleum.

DISCUSSION.

Dr. ARMSTRONG and Dr. COLLIE both drew attention to the possible formation of a hexamethylene compound by the reduction of the diketone diacetylpentane, and asked what evidence other than synthetical established the constitution of the reduction product.

Dr. KIPPING, while admitting that at present there was no such evidence, contended that the formation of a hexamethylene compound was altogether improbable.

10. "The Osmotic Pressures of Salts in Solution." By R. H. ADIE, M.A.

This paper contains the experimental results of an investigation of the osmotic pressures of salts in solution by direct observation, by the method of Pfeffer. The results are arranged under five headings.

1. *Boyle's Law applied to solutions.* The observations are plotted out with osmotic pressures for ordinates and concentrations (in terms of grm. molecules per litre) for abscissæ. The salts observed were potassium and sodium nitrates, potassium iodide, potassium sulphate, potash alum, potassium ferrocyanide and cobalticyanide, and a few others. The results obtained show that the osmotic pressures do not vary directly as the concentrations, but take a definite curved form, approaching Ostwald's line of no dissociation at two points, and receding from it elsewhere. Potash alum gives the nearest approach to a straight line of the salts examined.

2. *Charles's Law applied to solutions.*—Only one experiment yielded any result, and that was confirmatory of the correctness of applying Charles's Law to solutions.

3. *Influence of bases on osmotic pressures.*—No definite influence can be attributed to the base, except that the salts of some bases, e.g., soda, appear to be more readily dissociated by water than those of others, e.g. potash.

4. *Influence of acids on osmotic pressures.*—In the case of inorganic acids, no very definite influence can be detected; though the equivalents of the salts of monobasic acids give in general higher osmotic pressures than those of the salts of dibasic acids. In the case of organic acids an increase in the molecular weight of

homologous acids increases the osmotic pressure, and a ring nucleus gives a higher osmotic pressure than an open chain.

5. *Avogadro's Law applied to salts in solution.*—The author examines and compares the differences between the observed results and those calculated on the assumption that Avogadro's Law applies to salts in solution, and suggests that they may be due, as in Crookes's hypothesis, to the existence of simple and complex molecules in solution, as well as to the formation of water compounds in the solution. This hypothesis does not appear to require so large a modification of ordinary chemical ideas as that of Ostwald and Arrhenius.

11. "A Direct Comparison of the Physical Constants Involved in the Determination of Molecular Weights by Raoult's Method." By R. H. ADIE, M.A.

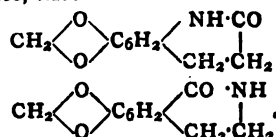
In this paper the author tries to connect the constants of Raoult's method of determining molecular weights of a substance in solution with those ascertained by direct observation of the osmotic pressure of the same solution. Also, by the same method of Raoult, to connect the osmotic pressure with the gaseous pressure of any substance in solution. The substances chosen are potassium iodide and ammonia. The solutions of potassium iodide and ammonia are compared by means of the lowering of the freezing point, and then the osmotic pressures of the same solutions of potassium iodide are given. The author shows that the constants obtained by the two methods do not agree, and suggests an hypothesis to explain the same, which is given above.

DISCUSSION.

Mr. PICKERING said that the numerous results brought forward by Mr. Adie could not fail to be of value. They seemed to afford fresh proof of the irregularities almost invariably shown by the properties of solutions, where, according to the physical theory, there should be nothing but regularity and uniformity. It was to be regretted that the determinations had not been pushed further into the region of dilute solutions, for it was here that some of the most surprising irregularities existed, and it was here that the existence of such must tell most strongly against any purely physical theory. Mr. Adie had touched on one of the most fundamental objections to the present physical theory of solution—the existence of osmotic pressure—for this is due to the impermeability of a membrane to the dissolved substance; and how can it be contended that if the molecules of the latter were single, and still more if they were dissociated into ions, they cannot get through holes which the water molecules have no difficulty in threading?

12. "Derivatives of Piperonyl." By FREDERICK M. PERKIN.

The author describes the results of experiments made with the object of determining the constitution of the compound $C_{10}H_9NO_3$ obtained by his brother from berberine (*Trans.*, 1890, p. 992), a knowledge of which was essential to the determination of the nature of this alkaloid; two formulæ would account for the properties of the substance, viz.:—



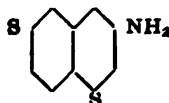
The second of these is found to be applicable to the substance in question. In the present paper, the author describes the preparation of the compound represented by the first formula from piperonal. On heating a mixture of nitropiperonal, acetic anhydride, and sodium acetate, an acid was obtained identical with that formed on nitrating the piperonylacrylic acid of Lorenz. On reduction with ferrous sulphate, this nitro-acid is converted into the corresponding amido-acid, but when zinc or tin and

maritic acid is used, the anhydro-derivative of the amido-acid is obtained.

The action of bromine on piperonylacrylic acid is described, and also the formation of a benzoin-like compound from piperonal and potassium cyanide.

13. "Studies on the Constitution of Tri-derivatives of Naphthalene, No. 9. Andresen's β -naphthylaminedisulphonic Acid." By HENRY E. ARMSTRONG and W. P. WYNNE.

According to Schultz (*Ber.*, vol. xxiii., page 77), naphthalene-1:3'-disulphonic acid on nitration yields a mixture of several nitronaphthalenedisulphonic acids. The chief product on reduction gives the so-called α -naphthylamine-1-disulphonic acid ($\text{NH}_2 : \text{SO}_3\text{H} : \text{SO}_3\text{H} = 1' : 1 : 3'$; *v.* Armstrong and Wynne, *Chem. Soc. Proc.*, 1890, 15] of the German patent 45776. Of the other acids, the production of which has been also noted by Bernthsen (*Ber.*, vol. xxiii., p. 3088, footnote), one yields on reduction, according to Schultz, a β -naphthylamine-disulphonic acid. As this was the first instance in which the formation of a *beta*-nitro acid by the nitration of a naphthalenesulphonic acid has been observed, the attention of the authors was directed to the determination of its constitution, and through the liberality of the Actiengesellschaft für Anilinfabrikation a considerable supply of the material remaining after the separation of the greater part of the acid was placed at their disposal for examination. After separation from the associated acids, and comparison with a specimen of the pure Andresen acid received from Dr. Schultz, the amido-acid was analysed by the hydrazine and Sandmeyer methods already described. When reduced by the hydrazine method it gave naphthalene 1:3' disulphonic acid, which was characterised by means of its chloride, $\text{C}_{10}\text{H}_6(\text{SO}_2\text{Cl})_2$, melting at 127° , and the derived 1:3' dichloronaphthalene melting at 48° . On treatment by the Sandmeyer process it was converted into a chloronaphthalenedisulphonic acid, the chloride of which, $\text{C}_{10}\text{H}_5\text{Cl}(\text{SO}_2\text{Cl})_2$, crystallised from benzene in radiate groups of flat needles melting at 174° , and on distillation with PCl_5 yielded 1:3:3' trichloronaphthalene melting at 80.5° . This acid, consequently, was identical with that obtained by the authors by sulphonating 2:2'- β -chloronaphthalenesulphonic with 20 per cent anhydrosulphuric acid (*Chem. Soc. Journ.*, 1890, 133). As a further proof of the identity of the two compounds, the chloronaphthalenedisulphonic chloride derived from the Andresen acid was hydrolysed by heating with dilute sulphuric acid at $250-270^\circ$ for several hours, with the result that β -chloronaphthalene melting at 59.5° was obtained. Combining these results it follows that the Andresen acid is a β -naphthylaminedisulphonic acid of the constitution—



The salts of this 2:4:2'- β -naphthylaminedisulphonic acid, and the mode of separation from the other naphthylaminesulphonic acids contained in the mixture, will be described when the examination of the nitration product of naphthalene 1:3' disulphonic acid has been completed.

CHEMICAL SOCIETY'S JUBILEE—1891.

February 24th.

(Concluded from p. 118).

W. CROOKES, F.R.S.,
President, 1887—1889.

The Seleniocyanides. 1851.

1. Original specimen of Seleniocyanide of Potassium.
2. Seleniferous deposit from the Sulphuric Acid Chambers at Tilkerode. From this deposit the Selenium used in the above research was prepared.

3. Residue left on distilling crude Selenium prepared from the above deposit. On examining this residue in the spectroscope a sharp green line was seen, which was afterwards proved to be due to a new element, Thallium.

Thallium and its Compounds. 1861.

4. Thallium, pure metallic, *in vacuo*. Thallium oxide, peroxide, chloride, sesquichloride, bromide, iodide, sulphide, cyanide, sulphocyanide, sulphate, nitrate, carbonate, acetate, oxalate, picrate, chlorate, perchlorate, chromate, bichromate, tartrate, bitartrate, benzoate, and potassium tartrate.

5. A prism of thallium glass, in which thallium replaces lead. Sp. gr. 4.75. Refractive index for the D line 1.751.

6. Crookesite, from Skrikerum, Norway. A selenide of thallium, copper, and silver.

	Per cent.
Thallium	17.25
Copper	45.76
Silver	3.71
Selenium	33.28
	100.00

7. Thalliferous Pyrites, from Millom, Cumberland.

8. Thalliferous Flue Dust, from Sulphuric Acid Works using thalliferous pyrites. (a) From Allhusen's Works, Newcastle. (b) From the Washington Chemical Works, Durham.

Repulsion resulting from Radiation. 1873.

9. Original Apparatus used in this investigation.

Pith ball balance in air, and *in vacuo*. The balls in air are apparently attracted, and *in vacuo* are repelled if a flame is brought near them.

Pith discs suspended horizontally.

Platinum bar suspended in tube of hard glass. This was heated to a high temperature while exhaustion was proceeding, to show that the repulsion does not depend on the presence of moisture.

Glass rods with mica ends *in vacua*, of various degrees of perfection.

Torsion balance to measure the force with which the blackened disc is repelled when exposed to radiation.

Pith bars with mirrors attached suspended (a) in air, (b) *in vacuo*. The blackened end of (a) is attracted and that of (b) repelled when a flame is brought near them.

The Radiometer. 1875.

10. The first Radiometer.

11. Early forms of Radiometers.

12. Lecture form of Radiometer.

13. Radiometers in which the source of heat is a platinum spiral inside the tube which is heated by an electric current.

14. Radiometers with vanes coated with different materials.

15, 16. Radiometers showing a different action according to whether heat or light falls on them. Certain bodies are more affected by luminous radiations than by the heat rays, while others are affected in the inverse order. If pairs of these substances in fine powder, are painted on alternate sides of the vanes of a radiometer, the rotation will be in one direction if the light of a candle is allowed to shine direct on them, and in the opposite direction if the light is first filtered through a plate of alum or a cell of water. One of these radiometers has its vanes coated on alternate sides with persulphocyanogen and copper oxalate, and the other radiometer has its vanes coated with chromic oxide and copper tungstate.

17. Radiometer with vacuum gauge attached.

18. First Radiometer made to investigate the effect of the shape of the vanes. The corners are turned up.

19. Radiometers in which the opposite sides of the vanes are of different shapes or are differently presented to the glass envelope.

Vanes inclined to the arms. Very thin mica vanes. Thicker mica vanes. Cone-shaped vanes. Cylindrical vanes. Cup-shaped vanes.

20. Apparatus in which the source of heat is a platinum wire.

21. Radiometers furnished with movable mica or metal screens, which can be jerked into different positions relatively to the vanes.

22. Double Bulb Radiometer to investigate the effect of the dimensions of the bulb. The vanes can be balanced in either bulb.

23. Radiometer to show that, if the vanes are held at rest by means of a magnet attached to them, the bulb, if free to move, will rotate.

24. A Spiral Radiometer of roasted mica blacked on the upper side.

25. A four-armed Metallic Radiometer with deep cups, bright on both sides.

26. A four-armed Radiometer, the vanes consisting of mica cups, bright on both sides.

27. A four armed Radiometer having clear mica vanes. The direction of motion being determined by the angle formed by the mica vanes with the inner surface of the glass bulb.

28. A vertical Radiometer, made with eight discs of mica blacked on one side, and the whole suspended on a horizontal axis which works in two glass cups. The motion of the radiometer is assisted on each side by driving vanes of aluminium blacked on one side.

Application of the Radiometer to Photometry.

29. Apparatus showing variations in the intensity of light on a divided scale.

Otheoscopes or Instruments in which the driving surface is not the glass of the bulb, but an interior disc, or surface which becomes heated.

30. Otheoscope.—A four-armed fly carries roasted mica vanes, and is mounted in an exhausted glass bulb like a radiometer. Fixed to the side of the bulb are three plates of clear mica, equidistant from each other in a vertical plane, but oblique to the axis. A candle brought near the fixed plates generates molecular pressure, which, falling obliquely on the fly, causes it to rotate.

31. Ctheoscope.—A large horizontal disc, revolving by the molecular disturbance on the surface of inclined metallic vanes, which are blacked on both sides in order to absorb the maximum amount of radiation.

Molecular Physics in High Vacua. 1878.

Original Apparatus used in this investigation :—

32. Apparatus to show the Dark Space round the Negative Pole. When the spark from an induction coil is passed through an ordinary vacuum tube, a dark space is seen round the negative pole. The shape and size of this dark space do not vary with the distance separating the poles; nor, only very slightly, with alteration of battery power, or with intensity of spark.

33. Apparatus to show the Green Phosphorescent Light of Molecular Impact. At very high exhaustions the dark space becomes so large that it fills the tube, and when German glass is used the sides are beautifully illuminated with a greenish yellow phosphorescent light.

34. Apparatus to show the Conveyance of the Molecular Streams to a Focus. The plate covered with calcium sulphide is furnished with a scale on which the "focal length" of the curved electrode is indicated.

35. Apparatus to show that the Paths of the Molecules are straight lines.

36. Apparatus to show the Projection of Molecular Shadows. The rays exciting green phosphorescence will not turn a corner, but radiate from the negative pole in straight lines, casting strong and sharply defined shadows from objects which happen to be in their path. The best and sharpest shadows are cast by flat discs, and not by narrow pointed poles; no green light is seen in the shadow itself, no matter how thin or whatever may be the substance from which it is thrown.

37. Apparatus to show Shadow of Object which is interposed in the Paths of the Molecules. The molecules which pass the aluminium cross make the glass phosphoresce so that a shadow of the cross appears.

38. Apparatus in which the Negative Pole is a Coin; the device is reproduced on the glass by the phosphorescence excited by the molecular streams.

39. Apparatus to show that the line of phosphorescent light excited by a molecular stream in a plate covered with calcium sulphide is deflected by a magnet, thereby proving that the paths of the molecules are affected by the presence of a magnet.

40. Apparatus to show the Mechanical Action of Projected Molecules. An actual material blow is given by the impinging molecules. A small vaned wheel being used as an indicator, by appropriate means the molecular shadow of an aluminium plate is projected on the vanes. When entirely in the shadow the indicator does not move, but when the molecular stream is deflected so that one half of the wheel is exposed to molecular impact it rotates with extreme velocity.

41. Paddle-wheel which can be rotated in either direction according as the molecular stream is directed to its upper or lower vanes by a magnet.

42. Electrical Radiometers. The vanes revolve when connected with the negative pole of an induction coil. At low exhaustions a velvety violet halo forms over each side of the vanes. On increasing the exhaustion the dark space widens out. On further exhaustion the dark space on the metallic side touches the glass, when positive rotation takes place.

43. Apparatus to show the Focus of Heat of Molecular Impact. Great heat is evolved when the concentrated focus of molecular rays from a nearly hemispherical aluminium cup is allowed to fall on a strip of platinum-foil, the heat sometimes exceeding the melting-point of platinum.

44. A disc is supported by a carbon rod resting on carbon supports which form a microphone. If a telephone be included in the circuit, the movement of the disc produced by the impact of a beam of light can be detected by the sound produced by the microphone.

45. Apparatus with Idle Poles to test the Electrification of Bodies interposed between the poles in the molecular stream.

46. Apparatus to test the effect of the Electrification of a Neighbouring Conductor on the molecular streams.

47. Apparatus to investigate the Shadow of a Vibratory Pendulum.

48. Apparatus with two Negative Poles. When one negative pole only is used lines of light are produced in the phosphorescent plate by the molecular streams. When both are employed simultaneously the lines shift in such a direction as to prove that the molecular streams repel each other.

Radiant Matter. 1879.

Original Apparatus used in this investigation :—

49. Vacuum Tube, with exploring pole, used in investigating the electrical condition of a highly exhausted tube when electrically excited.

50. Apparatus to show the action of the electrified walls of a vacuum tube on the stream of Radiant Matter, projected from the negative pole. In the wide part of the tube the stream of Radiant Matter follows its normal course straight from the negative pole, but in the narrow part of the tube so great is the attraction of the walls that the molecular stream widens out till it covers the whole screen.

51. Apparatus showing that the radiant molecules behave differently at a vacuum just short of non-conducting to what they do in ordinary high vacuum.

52. Apparatus showing the return of the exhausted molecules after having been shot off from the negative pole. The charged molecules pass through a small hole in a glass diaphragm, and turn a mill by their impact.

The returning molecules, passing through another hole, turn a second mill.

Apparatus to show that *Radiant Matter* is not *Radiant Electrode Matter*.

53. Apparatus showing that all the phenomena of *Radiant Matter*, such as projection of molecular shadows, mechanical energy, production of heat, and phosphorescence, can be produced in tubes without inside electrodes.

54. Apparatus used in experimenting on the Electrical Resistance of High Vacua.

55. Double vacuum tube of different electrical resistance. One side containing carbon, and the other side containing yttria.

56. Apparatus showing that the resistance of vacuum tubes is dependent on the material surrounding the poles.

Phosphorescence in High Vacua. 1879.

57. Apparatus to show the Phosphorogenic Properties of the Molecular Stream. Substances known to be phosphorescent under ordinary circumstances shine with great splendour when subjected to the negative discharge in a high vacuum.

58. Apparatus with cylindrical electrode to show phosphorescence produced in glass.

59. Apparatus with corrugated electrode. The molecular streams from the projections interfere and produce a pattern on the glass.

60. Tubes for the production of phosphorescence by means of the molecular stream on calcium sulphide.

61. Diamonds, various, in vacuum tubes. Under the influence of the induction spark these diamonds phosphoresce of different colours, according to their origin. Thus, Cape diamonds usually phosphoresce blue; Brazilian diamonds phosphoresce red, orange, blue, and yellow; Australian diamonds phosphoresce yellow, blue, and green.

62. Diamonds mounted in enamel. When subjected to the molecular stream they phosphoresce with blue, yellow, green, or apricot-coloured light.

63. Rubies. These stones phosphoresce with a brilliant red light.

64. Mixed stones which phosphoresce with various colours. The collection includes Diamonds, Rubies, Garnet, Topaz, Phenakite, and Spodumene.

65. Topaz.—Phosphoresces blue.

66. Sapphire.—Phosphoresces green.

67. Spinel.—Phosphoresces with a crimson light.

68. Phenakite.—Usually phosphoresces blue. Occasionally a crystal is found which phosphoresces yellow.

69. Pectolite.—Phosphoresces of a straw-colour.

70. Calcite.—Phosphoresces of an orange-colour.

71. Phosphorescent Calcite from Branchville, South Carolina. When heated in air it has the curious property of glowing strongly with a golden yellow light. In the *Radiant Matter Tube* this phosphorescence is very brilliant.

72. Spodumene. Phosphoresces of a yellow colour. A phosphorescing crystal of Spodumene has all the internal light cut off with a Nicol prism when the long axes of the Nicol and the crystal are parallel.

73. Dolomite.—A granular form from Utah; when scratched with a knife or struck with a pick it emits so strong a phosphorescent red light that the miners call it "Hell-fire Rock." In the *Radiant Matter Tube* it glows with a fine red light.

74. Zirconium Oxide, Calcined.—Phosphoresces with a bluish white light.

75. Strontium Oxide, Calcined.—Phosphoresces with a fine blue light.

76. Glucinum Oxide, Calcined.—Phosphoresces with a faint blue light.

77. Calcium Sulphide.—Phosphoresces blue, yellow, green, or red, according to the mode of preparation.

78. Zinc Sulphide (Sidot's hexagonal blende).—This is the most brilliantly phosphorescent body yet met with.

In the vacuum tube it begins to phosphoresce at an exhaustion of several inches below a vacuum. At first only a green glow can be seen; as the exhaustion gets better a little blue phosphorescence comes round the edges. At a high exhaustion, on passing the current, the green and blue are about equal in brightness, but the blue glow vanishes immediately the current stops, while the green glow lasts for an hour or more. Some parts of a crystalline mass of blende which, under the action of radiant matter, glow of a bright blue colour, give a green residual light when the current ceases; other parts which glow blue become instantly dark on stopping the current.

Electric Lighting by Incandescence. 1881.

79. Structureless cellulose for carbon filaments.

80. Incandescent electric lamps, with structureless carbon filaments.

81. The smallest electric lamp, diameter 3·8 m.m., weight 1·9 grains. 7·4 volts., 0·6 ampère, 1 C.P.

Radiant Matter Spectroscopy. 1883.

Apparatus and Specimens illustrating this investigation:—

82. Alumina in the form of a precipitate or crystallised as the Ruby, phosphoresces of a rich crimson colour, and when the light is examined in the spectroscope it is seen to consist essentially of one sharp line in the red.

83. Yttrium Sulphate.—Phosphoresces with a golden yellow light. Examined with a spectroscope gives a remarkable discontinuous spectrum.

84. Samarium Sulphate.—Phosphoresces with a red light, and gives a spectrum composed of three broad bands.

Specimens of Rare Earths and their Salts:—

Ceria.	Niobic acid.
Ceric oxalate.	Philippic (?) formate.
Decipia.	Tantallic acid.
Didymia.	Terbia.
Didymic oxalate.	Thoria.
Didymic sulphate.	Thoric oxalate.
Erbia (rose-coloured).	Thoric sulphate.
Gadolinia (Ya).	Ytterbia.
Lanthana.	Yttria.
Lanthanic oxalate.	Zirconia.
Thulia (with erbia).	

Specimens of Yttria from the following minerals:—

Gadolinite.	Hielmite.
Samarskite.	Sipyrite.
Xenotime.	Arrhenite.
Monazite.	Fluocerite.
Euxenite.	Clévite.

Specimens of Minerals containing Rare Earths.

87. Gadolinite. The largest known crystal in the world. It weighs 40 lbs., and contains nearly 50 per cent of Yttria.

88. Samarskite. Various specimens.

89. Allanite. A very large specimen.

90. Thorite and Orangeite in crystals.

91. Eudyalite.

92. Orthite.

93. Alvit.

94. Rhabdophane.

95. Fergusonite.

96. Columbite.

97. Hjelmit.

Genesis of the Elements. 1886.

98. A Model Lemniscate Curve, illustrating the Presidential Address delivered before the Chemical Society, March 28th, 1886.

Elements and Meta-Elements. 1889.

Specimens illustrating the Presidential Address delivered before the Chemical Society, March 21st, 1889.

99. Vacuum tubes containing new earths separated from Yttria by continued fractionation. Under the influence of molecular bombardment these earths phosphoresce brightly, and give spectra consisting essentially of one or two bright lines.

100. The following Table gives the mean wave-length of certain definite absorption-bands or lines in the phosphorescent spectra of presumably new elements which have been separated from the earth yttria by fractional precipitation, repeated many thousand times:—

Position of lines in the spectrum.	Mean wave-length of band or line.	Provisional name.
Absorption-bands in {	443	Da
violet and blue .. {	475	Sβ
Bright lines in		
Deep blue	482	Gα
Green	564	Gγ
Citron	574	Gδ
Yellow	597	Gε
Orange	609	Sδ
Red	619	Gζ
Deep red	647	Gη

(Exhibited by Mr. Crookes.)

GEORGE FOWNES, F.R.S.

A.D. 1815—1849).

One of the early Secretaries of the Society.

Oil of Bran.—This is a portion of the oily liquid obtained by distilling bran with diluted sulphuric acid, from which, in the year 1845, Fownes, the first Professor of Chemistry to the Pharmaceutical Society, isolated a substance which he called "furfural" (*furfur*, bran, and *oleum*, oil—*Phil. Trans.* 1845).

Furfurine.—This derivative of furfural, isomeric with furfuramide, was discovered by Fownes, by whom the present specimen was prepared.

Furfurine Nitrate.—Specimen prepared by Fownes. (Exhibited by Prof. Dunstan.)

EDWARD DANIELL, F.R.S.,

Professor of Chemistry in King's College.

Cell of Daniell's Original Battery.

Daniell's Constant Battery (large cells).

Daniell's Gas Battery.

Daniell's Hypometer on Air-Pump Receiver,

Daniell's Original Pyrometer, with iron case for heating substances in.

(Exhibited by the Council of King's College, London.)

THOMAS THOMSON, F.R.S.

Small Chemical Balance, originally belonging to Prof. Thomas Thomson. F.R.S.

(Exhibited by Prof. J. M. Thomson.)

THOMAS ANDREWS, F.R.S.,

Professor of Chemistry in Queen's College, Belfast.

Collection of Apparatus used by the late Dr. Andrews in his researches:—

1. Six straight Tubes used in experiments on Ozone.
2. Two bent Tubes employed for the same purpose.
3. Two Tubes used in attempts to liquefy the "permanent" gases.
4. A compression Apparatus used in his experiments on the continuity of the liquid and gaseous states.
5. The first Apparatus with which Andrews worked on this subject. (The compression screw and the tube containing carbonic anhydride are not the original ones.)
6. A Tube ready calibrated for the above.
7. A Wooden Curve Model, showing the changes of volume which carbonic anhydride experiences under different conditions of temperature and pressure.
8. A Calorimeter used in determinations of the heat of combination.

(Exhibited by Prof. Letts, Queen's College, Belfast.)

Later and perfected forms of Apparatus used by Andrews in his researches on the critical point of gases and liquids.

(Exhibited by the Science and Art Department, South Kensington.)

JAMES PRESCOTT JOULE, D.C.L., F.R.S.

Model of the Calorimeter used by him in the determination of the Mechanical Equivalent of Heat.

(Exhibited by the Science and Art Department, South Kensington.)

WALTER WELDON, V.P.C.S.

Complete model of a plant for his chlorine process.

(Exhibited by the Science and Art Department, South Kensington.)

DR. EDWARD SCHUNCK, F.R.S.,

Sometime Vice-President of the Society.

Indirubin, crystallised. — The red colouring matter always formed by decomposition of indican along with indigo-blue, with which it is isomeric, probably identical with the indigo-red of Berzelius. Dyes red, or rather purple, using the same process as that employed for dyeing blue with indigo-blue.

Chrysammic Acid. — First obtained by the action of nitric acid on aloes in 1841. Is a nitro-compound of a di-oxyanthraquinon. Magnesium chrysammate is the most beautiful of its salts.

Magnesium chrysammate.

Anthrarufflavic Acid and *Iso-anthrarufflavic Acid*. — These are isomerides of alizarin which are formed during the process of the artificial production of the latter. As they are not in the least tinctorial their presence is not desirable, and their formation is prevented as much as possible.

Anthrarufin. — Another isomeride of alizarin formed by the action of sulphuric acid on meta-oxybenzoic acid.

Flavopurpurin. — A trioxyanthraquinon formed by suitable means from anthrarufflavic acid. It is used in dyeing. The corresponding purpurin from iso-anthrarufflavic acid is Dr. Perkin's anthrapurpurin.

Tribromflavopurpurin.

Diacetylflavopurpurin.

Phyllotaonin. — Remarkable as being the first derivative of chlorophyll obtained in well-defined measurable crystals. All products previously obtained from chlorophyll were either amorphous or merely crystalline. Ethyl-phyllotaonin and methyl-phyllotaonin are pretty bodies, the solutions of which show a distinct absorption spectrum.

Ethyl-phyllotaonin.

Methyl-phyllotaonin.

(Exhibited by Dr. Schunck.)

WILLIAM FRANCIS, PH.D., F.L.S., F.C.S.

Liebig's Combustion Furnace and *Potash Bulbs* for organic analysis. The first specimens brought to this country from Giessen, by Dr. Francis, in the year 1842.

Coloured Daguerreotype by Beard. This was one of the first ever taken, and was done at the same time as that of Mr. Robert Warington.

(Exhibited by Dr. Francis.)

ROBERT WARINGTON, F.R.S.

The Jubilee Album, containing the Letters received by Mr. Warington in reply to the circular inviting persons to become Members of the proposed Chemical Society, with various printed papers relating to the formation and early history of the Society and Portraits of 44 of the Original Members.

The Obligation Book of the Chemical Society, containing the signatures of Fellows on joining the Society. On page 1 are the signatures of 53 Original Fellows.

Early Photographs of W. T. Brand, M. Faraday, G. Fownes, T. Graham, W. Gregory, Justus von Liebig, R. Phillips, and R. Warington.

Early Daguerreotype, one of the first taken in London. Portrait of R. Warington.
Berzelius's Filter-Paper. Portion of a parcel sent to Dr. Ed. Turner before 1837.
Dalton's 'Graphic Formulæ', published 1835.
 (Exhibited by Mr. R. Warington.)

GEORGE MATTHEY, F.R.S.

Platinum Snuff-box. The lid stamped to show the duility of the metal; made about the year 1816, by the late P. N. Johnson, F.R.S., founder of the firm of Johnson, Matthey, and Co., and used by him until his death in 1864.

Another, made in St. Petersburg about the year 1830. Platinum Coin or Medal, made in St. Petersburg, 1826. Nugget of Native Platinum, found in the Ural district very early in the present century. Weighs 166 ounces.

Specimen of Jacotinga from the Brazils, in which the greater portion of the palladium was found associated with the gold-dust obtained from it.

Specimens of the six metals of the platinum group, namely, platinum, palladium, rhodium, ruthenium, iridium, and osmium.

(Exhibited by Mr. George Matthey.)

JOHN SPILLER, F.C.S.

Frame of Early Photographs.
 (Exhibited by Mr. Spiller.)

Portraits of Past Presidents of the Chemical Society:—
 T. Graham (1841—1843, 1845—1847). W. Aikin (1843—1845). W. T. Brande (1847—1849). R. Phillips (1849—1851). C. Daubeny (1851—1853). P. Yorke (1853—1855). W. A. Miller (1855—1857, 1865—1867). L. Playfair (1857—1859). B. C. Brodie (1859—1861). A. W. Van Hofman (1861—1863). A. W. Williamson (1863—1865, 1869—1871). W. De la Rue (1867—1869, 1879—1880). E. Frankland (1871—1873). W. Odling (1873—1875). F. A. Abel (1875—1877). J. H. Gladstone (1877—1879). H. E. Roscoe (1880—1882). J. H. Gilbert (1882—1883). W. H. Perkin (1883—1885). H. Müller (1885—1887). W. Crookes (1887—1889).

Robert Warington, First Secretary of the Society.

Henry Watts, Editor of the Journal, and Librarian of the Society.

G. Longstaff, Founder of the Longstaff Medal.

Justus von Liebig, sometime Foreign Member.

Prof. Mendelejeff, Foreign Member.

PHYSICAL SOCIETY.

February 27th, 1891.

Prof. W. E. AYRTON, F.R.S., President, in the chair.

PROF. A. GRAY was elected a member of the Society.

THE following communications were read:—

"*Proof of the Generality of Certain Formulæ Published for a Special Case by Mr. Blakesley. Tests of a Transformer.*" By W. E. AYRTON, F.R.S., and Mr. J. F. TAYLOR.

In 1888, Mr. Blakesley published a number of formulæ relating to the measurement of power, &c., in alternating current circuits by means of electro dynamometers, one of which had its two coils independent, and placed in different circuits. These formulæ were deduced on certain assumptions, the chief ones being that the currents and magnetisations varied harmonically, and that the magnetic stress in the iron was proportional to the ampère turns. The present paper shows that the above assumptions are not necessary to the truth of the resulting formulæ. To take the case of a transformer:—Let alternating current ammeters be placed in the primary and secondary circuits, and a direct reading "split dynamometer" have a coil in each circuit. Let D_p , D_s , and D_{ps} be the respective readings of these

instruments, then, whatever be the law of variation of the currents,—

$$\left. \begin{aligned} D_p &= \sqrt{\frac{1}{T} \int_0^T A_p^2 dt}, \\ D_s &= \sqrt{\frac{1}{T} \int_0^T A_s^2 dt}, \\ \text{and } D_{ps} &= \sqrt{\frac{1}{T} \int_0^T A_p A_s dt} \end{aligned} \right\}$$

where A_p and A_s are the values of the primary and secondary currents at any instant, and T the time of one complete alternation.

If i be the total induction in the core, P and S the number of turns of wire on the primary and secondary respectively, V_p and V_s the terminal pressures, ρ the resistance of the primary coil, and s the resistance of the whole secondary circuit, then the following equations hold at any instant:—

$$\left. \begin{aligned} V_p &= \rho A_p + P \frac{di}{dt} \\ \frac{di}{dt} &= \frac{s}{S} A_s \end{aligned} \right\}$$

Therefore—

$$V_p = \rho A_p + \frac{P}{S} s A_s;$$

multiplying both sides by A_p we get—

$$A_p V_p = \rho A_p^2 + \frac{P}{S} s A_p A_s,$$

and integrating from $t=0$ to $t=T$, and taking the mean,

$$\frac{1}{T} \int_0^T A_p V_p dt = \frac{\rho}{T} \int_0^T A_p^2 dt + \frac{P}{S} \frac{s}{T} \int_0^T A_p A_s dt,$$

or Watts in primary = $\rho D_p^2 + \frac{P}{S} s D_{ps}$, quite independent of the laws of variation of A and V .

The power lost in heating the iron core was also shown to be—

$$s \left(\frac{P}{S} D_{ps} - D_s^2 \right)$$

Other formulæ, such as that given by Mr. Blakesley expressing the primary volts in terms of the dynamometer readings, are shown to be true generally.

On the subject of transformer magnetisations, the authors state that it is desirable not to speak merely of the ampère turns, but also of the self-induction, for they have reason to believe that the magnetising value of an ampère-turn varies. Defining the self-induction of the secondary by the equation $L_s = \frac{dN}{dA_s}$, N being the total flux through

the secondary, they show geometrically (assuming harmonic variations) that if L_s diminishes, the efficiency increases, and, at the same time, the phase angle, θ , between the primary and secondary currents, and the magnetic lag, ϕ , decrease. On comparing this theoretical deduction with the results of experiment, they find a good agreement, as will be seen from the following table:—

Frequency.	Efficiency.	L_s .	θ .	ϕ .
160	96.3%	0.0017	113°	0° 24'
"	92%	0.0368	169°	18° 24'
"	85.4%	0.1241	174° 6'	45° 36'

The above tests were made on a Mordey transformer, kindly lent by the Brush Electrical Engineering Corporation.

Similar results were obtained in different sets of experiments. It was also noticed that as the secondary current is increased, the efficiency rises to a maximum and then diminishes, whilst L_s , θ , and ϕ diminish and then rise again; the current which gives the maximum efficiency coinciding almost exactly with that which gives the minimum values to L_s , θ , and ϕ .

The methods employed in making the tests are described in the paper, and the formulæ used in working out the results are there demonstrated. Amongst the facts deducible from the experiments are the following:—

1. With constant frequency, the ratios $\frac{V_s}{V_p}$ and $\frac{D_s}{D_p}$ increase as the primary volts rise.
2. With frequency constant, and primary volts constant, $\frac{V_s}{V_p}$ decreases and $\frac{D_s}{D_p}$ increases as the secondary current increases.
3. With constant secondary current, L_s decreases as the primary volts are increased.
4. With small constant secondary currents, the efficiency diminishes as the frequency increases.
5. For large secondary currents the efficiency is approximately independent of the frequency.
6. Shunting the secondary with a condenser increases the efficiency.

"Further Contributions to Dynamometry." By T. H. BLAKESLEY, M.A.

The object of Mr. Blakesley's paper was, in the first place, to show what sort of physical quantities could be advantageously evaluated by using electro-dynamometers of two coils of low resistance in circuits conveying electric currents. The meaning of a dynamometer reading was explained to be the mean value of the product of two currents, either steady or undergoing any periodic variations, with sufficient rapidity. In mathematical language, such an instrument measured—

$$\frac{1}{T} \int_0^T C_1 C_2 dt;$$

where C_1 and C_2 were the instantaneous values of the currents in the two coils, including, of course, the common case where these currents are identical.

Any physical quantity whose value was such a product, $C_1 C_2$, multiplied into something which was independent of the time, and which therefore on integration came outside the integrator, was well adapted to have its mean value given by such instruments. Power was such a quantity, being merely (Current)² × resistance. The square of an E.M.F. was another such quantity, but he did not wish to restrict the method to such evaluations.

It follows that any quantity whose instantaneous value can be expressed by terms each quadratic in current, and whose other factor was independent of time, could have its mean value expressed in dynamometer readings. In addition, the particular place and mode of coupling of the dynamometers was indicated by the instantaneous equation, as well as the factor to be applied to such reading. Thus the equations are made to indicate the practical arrangement to be adopted, and the use to be made of the observations in each case.

Examples were given for the cases of transformers in series and parallel, and special applications of the method were suggested in the measurement of the power employed in such diverse apparatus as voltmeters subject to direct or variable currents of any sort, welding machines, parallel generators, tuning-fork circuits, vacuum discharges, and imperfect condensers. For parallel generators the power of each could be separately estimated, and in the case of electric welders the power employed in the welding circuit was shown to be measurable without introducing any resistance whatever into that circuit.

Mr. J. SWINBURNE said the author's assumption that there is no back or forward E.M.F. in the primary and secondary circuits of transformers, except that due to $\frac{di}{dt}$, where i is the total induction in the core, was unwarrantable, for in all real transformers there was a "drop" due to waste field, and this made the split dynamometer method useless. It makes the full load efficiencies too high; and this, he thought, accounted for the extraordinary results obtained by Prof. Ayrton and

Mr. TAYLOR. If a dynamometer be used at all, it should, he said, be used as a wattmeter, the moving coil of one turn being joined in series with a non-inductive resistance and put as a shunt to the primary. The power absorbed by the instrument itself should be then determined, and the power given out by the secondary measured by the same instrument, if the secondary be not non-inductive. Any errors due to self-induction in a wattmeter are, he said, equally present when it is called a split dynamometer, and, in addition to this, the wattmeter as a split dynamometer precludes the possibility of measuring power.

Mr. MORDEY said the results obtained by Prof. Ayrton and Mr. Taylor confirmed experiments he had made himself by an entirely different method, for he found that the losses in the iron decreased considerably as the secondary current increased, and this gave increased efficiency. In his experiments he kept the load constant until the transformer attained a steady temperature, and then substituted a direct current for the alternating one, varying its strength until the same steady temperature was maintained. The power thus supplied is a measure of the loss in the transformer under the working condition. A 6-kilowatt transformer tested by this method gave a loss of 110 watts at no load, and at full load 205. Of this 205, 176 was accounted for by the loss in the copper coils, leaving only 29 watts as the iron losses at full load. Figures which he quoted from Prof. Ayrton and Mr. Taylor's paper showed the same general result.

A "Note on Electrostatic Wattmeters," by Mr. J. Swinburne, and a paper on "Interference with Alternating Currents," by Prof. W. E. Ayrton, F.R.S., and Dr. Sumpner, were postponed.

ROYAL INSTITUTION OF GREAT BRITAIN General Monthly Meeting, March 2, 1891.

WILLIAM CROOKES, F.R.S., Vice-President, in the Chair.

MISS EMILY ASTON, B.Sc.; Henry Daw Ellis, M.A.; Francis Fowke; Augustus William Gadesden, J.P.; Miss Emily Dorah Locock; Signor Alberto Randegger; The Hon. Frederick Hamilton Russell; and John Wilson Walter were elected Members of the Royal Institution.

The Presents received since the last meeting were laid on the table, and the thanks of the Members returned for the same.

NOTICES OF BOOKS.

Sewage Treatment; or, the Purification of Water Carried Sewage. By H. LEONARD LINNELL, Ass. Mem. Inst. C.E. Bolton: Tillotson and Son.

FROM the small bulk of this work the various methods of dealing with sewage cannot be very fully described. The author very properly abstains from recommending any one system as universally applicable. For towns on the seaside—and he might have added, for those on tidal rivers—he justly condemns all devices for impounding the sewage and letting it out during ebb-tide. Concerning inland towns, he ventures on the statement that chemical precipitation processes have hitherto failed to effect the needful degree of purification.

For villages and public buildings he makes no mention either of the pail system or the dry-closet treatment.

In discussing the disposal of the sludge from the treatment of sewage, he mentions without merited condemnation the schemes of burning, first recommended, we believe, by the late General Scott, and that of conveying it out into the sea. Both these methods, as far as the mere waste of plant-food is concerned, are fully on a level with the old system of letting the sewage flow simply into

the nearest river, as it was done in London before the construction of the intercepting sewers.

Mr. Linnell is in favour of keeping the storm-water distinct from the sewage properly so called. This system has everything in its favour except the cost of a double system of sewage. The author's proposal to let the top water escape over a weir when the sewage reaches a certain height cannot be recommended, as, especially in a sudden storm after a long duration of dry weather, the overflow water contains a very large share of the suspended impurities.

The proposal to exclude "the refuse from chemical works, tanneries, dye-works, &c.," from the sewers is quite justifiable in theory. But what is to be done with such waste waters? They cannot be permitted to flow into the streams, nor to collect in ponds.

The precipitation processes described are not numerous, and as a rule they find too favourable a judgment. Some few errors in points of fact are met with; but had the author visited all the towns where the processes mentioned are in action and used his eyes and nose in conjunction, we think he would have found good reason to alter his opinion.

The author has certainly compressed into a very brief compass a remarkable quantity of information concerning sewage and its treatment.

Heat as a Form of Energy. By ROBERT H. THURSTON, Director of Sibley College, Cornell University. London: William Heinemann.

THE present work is the third volume of "Heinemann's Scientific Handbooks," and reproduces the general preface to which we have already called attention. There is also a special preface, the writer of which speaks of the precincts ascribed "to the physicist and the man of science." It is generally held that the physicist is one kind of the man of science. In this same preface the labours of the old philosophers receive but scant justice. We read of "the discovery of one logical fact and one physical truth after another." Surely the inquirer may here ask what is the meaning of a "logical fact?"

In the body of the work the author treats successively of the "Philosophers' Ideas of Heat," the Science of Thermodynamics, Heat-Transfer and the World's Industries, Air and Gas-Engines, their Work and their Promise, the Development of the Steam-Engine, and winds up with a summary. The view here given of heat and its laws is fully in accordance with the present state of our knowledge, and may therefore be accepted by the student as sound and trustworthy. On this very account it will call forth the wrath of the so-called "substantialists," a school of scientific heretics who have arisen in America, and who regard heat, and, we believe, even sound, as not modes of motion but substances. Mr. Thurston seems, however, if we may use the expression, to have his centre of gravity not so much in science as in industrial art. Hence he indulges somewhat magniloquently in the glorification of inventors. He forgets that in certain cases the good and the evil of invention are very nearly balanced, and that in others the latter may preponderate. Mechanical devices doubtless play the part formerly assigned to slaves; but like slaves they sometimes reduce those who are not their owners to a position similar to that of the former "mean whites" in the "slave States" of America.

We must enter our protest against a view here expressed:—"The fact illustrates a common experience—that practice and invention very often, if not generally, precede science, the latter coming in later to explain a result felt out by the inventor, or perceived by him by that peculiar intuition which is his birthright." The intuition of the inventor in lack or in defiance of the teachings of science leads sometimes to strange results. But putting this on one side, we must urge that as far as chemical inventions are concerned, their authors as a rule proceed on strictly

scientific principles. The coal-tar colours are not the fruit either of "practice or of intuition."

In conclusion, we may say that to a numerous class this work will prove both welcome and useful. The index is very imperfect.

CORRESPONDENCE.

IMPURE POTASSIUM SULPHOCYANIDE.

To the Editor of the Chemical News.

SIR,—In working recently with a specimen of potassium sulphocyanide, I became suspicious of its purity. To test this I estimated its percentage of sulphur, which was found to be only 10.1. Pure potassium sulphocyanide contains 32.95 per cent. About 150 grms. of the salt were therefore taken, dissolved in water, and re-crystallised in vacuo. The first crop of crystals, about 40 grms., was rejected. The next crop was examined and found to consist of small, well formed cubes, containing 10.22 per cent of sulphur. Since potassium sulphocyanide crystallises in long slender prisms, the cubic form of these crystals led me to look for chlorides. The following method was devised to separate and estimate any chlorine present. The impure salt was oxidised with excess of permanganate. The hydrocyanic acid formed during the oxidation was then got rid of by continued boiling with nitric acid. I then estimated the chloride present in the usual manner with silver nitrate.

The mean of three determinations gave 28.75 per cent of chlorine.

Three fresh samples of sulphocyanide were then obtained from three different makers, and examined by the above method. In each case only the merest trace of chlorine was found.

Calculating the chlorine found in the impure salt, into potassium chloride, and the sulphur into potassium sulphocyanide, we find—

KCl	60.44 per cent.
KCNS	31.01 ..
	91.45

As, except a trace of sulphate, no other impurities were found, it is probable that during the boiling with nitric acid some of the chlorine was lost. The above method does not, therefore, pretend to quantitative accuracy, but is a rapid and convenient method of discovering and approximately estimating chlorine in sulphocyanide.

Probably a considerable stock of the impure specimen has been cast upon the market: I think it well, therefore, to draw the attention of chemists to chlorine as a possible impurity in commercial sulphocyanide.

It may also be worthy of notice that in the presence of a large proportion of alkaline chloride, potassium sulphocyanide crystallises in cubes.—I am, &c.,

JAMES HENDRICK.

Chemical Laboratory, King's College, London.

ATOMIC WEIGHTS.

To the Editor of the Chemical News.

SIR,—With reference to the recent re-determinations of atomic weights in the platinum group, I should like to point out to readers of the CHEMICAL NEWS who may be in the habit of using Mr. Johnstone's useful little book, the "Analyst's Laboratory Companion," that the old erroneous weight of platinum is there given, viz., 197.2 instead of 194.3. The weight of osmium also is given as 198.5 instead of 190.3. The latter error is of course less material to the analyst, but it is very desirable that the

exact equivalent of such a reagent as platinum should be used in calculating the results of our analyses.—I am, &c.,

F. H. P. C.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxii., No. 8, February 23, 1891.

The Isolation of the Glycolytic Ferment of the Blood.—R. Lépine and Barral.—The experiment of the authors proves that the glycolytic power of the blood cannot be considered as a vital property of the albumen of the blood. In the series of three liquids, the serum, the first washings, and the second washings, the albumen decreases enormously, whilst the glycolytic power increases in the liquid and decreases in the globules. This transfer of the glycolytic power from the globules into the washing-water argues in favour of a soluble ferment.

On the Spectrum of α -Lyrae.—H. Deslandres.—The author, in opposition to Mr. Fowler, finds that the K ray of calcium in the spectrum of the star appears fine, distinct, and manifestly single; the nearest ray is at the distance of $\frac{1}{10}$ millimetre.

Testimonial to Professor Stas.—The Royal Belgian Academy is opening a subscription to present a gold medal to J. S. Stas on May 5th, by occasion of the 50th anniversary of his mastership of the Science section of the Belgian Academy.

The Compressibility of Mixtures of Air and Hydrogen.—Ulysse Lala.—The mixtures studied contained, respectively, 16.38, 28.12, 33.08, 39.28, and 49.89 per cent of hydrogen. The compressibility of mixtures in which the proportion of hydrogen increases from 16.31 is intermediate between those of air and of hydrogen for initially feeble pressures which increase with the proportion of hydrogen, and may rise to 175 c.m. of mercury for a mixture containing 49.89 per cent of hydrogen. But this compressibility deviates from Mariotte's law in the same direction as does that of hydrogen.

Position of the Luminous Vibration.—M. Carvallo.—The author's conclusions are that the laws of double refraction are not altered by dispersion. Calculation shows that M. Sarrau's system possesses the property that Briot's terms of dispersion do not introduce any perturbation in the laws of monochromatic double refraction, and that it is the only known system possessing this property.

Solubility of Potassium Bitartrate.—Ch. Blarez.—The solubility of cream of tartar in water, which is a function of the temperature θ , may be calculated by the quantity of the substance Q dissolved in 100 grms. of solution $Q\theta = 0.351 + 0.00151\theta + 0.000539\theta^2$. Its solubility in water is decreased by the presence of potassium chloride.

Transformation of Starch into Dextrine by the Butyric Ferment.—A. Villiers.—Besides certain substances formed in very small quantities, the chief products of fermentation are dextrines not attacked by *Bacillus amylobacter*.

Distribution of Sodium Chloride according to Altitude.—A. Muntz.—The author mentions that in Alpine pastures sheep, &c., can smelt salt. The rain-water and the herbage of elevated regions are much poorer in sodium chloride than those of the lowlands,

and the milk and the blood of animals feeding on the mountains contain a decidedly less proportion of the same salt than do those of similar animals from the plains.

Revue Générale des Sciences Pures et Appliquées.

Vol. ii., No. 2, January 30, 1891.

Photography of Objects at a Great Distance by the Intervention of the Electric Current.—Marcel Brillouin.—The author points out a difficulty which he thinks for the present insurmountable. To produce a luminous image, distinct to the naked eye, of 4 centimetres in diameter, the transmitting apparatus must completely obey the changes of illumination to which it is submitted in less than $\frac{1}{1000000}$ of a second in round numbers.

Annual Review of Applied Chemistry.—This consists of two distinct memoirs on the great chemical industries by Dr. G. Lunge, and on colouring matters and organic products by Ph. A. Guye. In the former are summarised an account of the invention of nickel oxychloride by Mond, Langer, and Quincke; remarks on water-gas; the recent improvements in the production of oxygen from air by the intervention of baryta, and by the ignition of a mixture of lead oxide and lime carbonate. The United Alkali Company is next discussed, and new methods of obtaining bleaching-lime, or of bleaching without the use of this compound, e.g., by electrolysis, are considered. In the paper on colouring matters it is stated that the red "de Saint Denis" is more brilliant than turkey red. Diamido azoxybenzene may be diazotised in each of its two groups NH_2 ; on causing the diazo compound formed to react upon α -sulpho α -naphthol the splendid scarlet colour just mentioned is formed. Concerning indigo, it is remarked that in spite of recent improvements the synthetic compound has not yet dethroned the natural product, and that the task of the assailants become from day to day more difficult. The yield of the plantations have been improved by a judicious selection of species. According to Schrottky there is still a possibility of utilising the natural product in a better manner by hindering or regulating certain phenomena of fermentation which take place in the vats at the cost of the colouring matter.

Bulletin de la Société Chimique de Paris.

Series 3, Vol. iv., No. 9.

This issue contains no original papers.

MISCELLANEOUS.

The Chemical Laboratory of Wiesbaden.—The Chemical Laboratory of Geh. Hofrath Prof. Dr. Fresenius at Wiesbaden enjoys a very large attendance. In the winter term, 1890/91, there were 81 students on the books. Of these, 61 were from Germany, 4 from England, 3 from Austria, 3 from Russia, 3 from Spain, 2 from North America, 1 from Luxemburg, 1 from Belgium, 1 from France, 1 from Norway, and 1 from Bulgaria. Besides the director, Geh. Hofrath Prof. Dr. R. Fresenius, there are engaged as teachers in the establishment Prof. Dr. H. Fresenius, Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. G. Frank, and Architect Brahm. The assistants in the instructional laboratory are 2 in number, in the private laboratory 17, in the Versuchsstation 2. The next summer term begins on the 24th of April. During the last term, besides the scientific researches, a great number of analyses were undertaken in the different departments of the laboratory, and in the Versuchsstation on behalf of manufacture, trade, mining, agriculture, and hygiene.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Removing Ink.—Can you inform me of any bleaching agents or chemicals that will remove writing and printing ink from paper? I have tried muriatic, also oxalic, acid applied with a brush, but find it does not quite remove the ink; so should be pleased to hear of something stronger, and the best means of applying the same. It does not matter if it bleaches the paper, so long as it entirely removes the ink and does not destroy the surface.—A. W.

MEETINGS FOR THE WEEK.

- MONDAY, 16th.**—Medical, 8.30.
— Society of Chemical Industry, 8. "Observations made in the Working of Vitriol Chambers," by W. Crowder. "The Chemistry of Whisky and Allied Products," by A. H. Allen.
— Society of Arts, 8. "Photographic Chemistry," by Prof. R. Meldola, F.R.S.
- TUESDAY, 17th.**—Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Society of Arts, 8. "Recent Development of Tasmanian Industries," by Sir Edward N. C. Braddon, K.C.M.G., Agent-General of the Colony.
— Royal Institution, 3. "The Structure and Functions of the Nervous System," by Prof. Victor Horsley, F.R.S.
- WEDNESDAY, 18th.**—Society of Arts, 8. "Harbours, Natural and Artificial," by F. H. Cheesewright.
— Meteorological, 7.
— Microscopical, 8.
- THURSDAY, 19th.**—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "Modern Chemistry in Relation to Sanitation," by Professor C. Meymoit Tidy.
— Chemical Society, 8. "The Molecular Refraction and Dispersion of various Substances," by Dr. J. H. Gladstone, F.R.S. "Contributions to our Knowledge of the Aconite Alkaloids—Part I. The Crystalline Alkaloid of *Aconitum napellus*," by Prof. Dunstan and Dr. W. H. Ince. "The Crystallographic Character of Aconitine from *Aconitum napellus*," by A. E. Tutton.
- FRIDAY, 20th.**—Quekett, 8.
— Physical Society, 5. "The Theory of Dissociation into Ions, and its Consequences," by S. U. Pickering, F.R.S. "Some Points in Electrolysis," by J. Swinburne. "The Variation of Surface-Tension with Temperature," by A. A. Selby, M.A. "On Magnetic Proof-pieces and Proof-planes," by Prof. S. P. Thompson.
— Royal Institution, 3. "Hydrophobia," by Prof. Victor Horsley, F.R.S.
- SATURDAY, 21st.**—Royal Institution, 3. "The Forces of Cohesion," by The Right Hon. Lord Rayleigh, F.R.S.

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LECTURES.

Experimental Chemistry (Inorganic) Prof. H. FRESENIUS, Ph.D.
Experimental Physics W. FRESENIUS, Ph.D.
Stoichiometry E. HINTZ, Ph.D.
Organic Chemistry E. HINTZ, Ph.D.
Chemical Technology E. BORGMANN, Ph.D.
Microscopy, with exercises in Micro-
scopic work { Prof. H. FRESENIUS, Ph.D.
.. .. . E. BORGMANN, Ph.D.
.. .. . W. FRESENIUS, Ph.D., and
.. .. . E. HINTZ, Ph.D.
Chemistry and Analysis of Foods Dr. med. G. FRANK.
Hygiene J. BRAHM.
Practical exercises in Bacteriology
Technical Drawing, with exercises

The next Session commences on the 24th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KRIZDEL'S Verlag, at Wiesbaden, or to the undersigned.

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THE CHEMICAL NEWS.

VOL. LXIII., No. 1634.

REPORT OF PROGRESS IN SPECTRUM WORK.*

By Professor HENRY A. ROWLAND.

DURING the past year or two a great deal of work has been done in the photography of the spectra of elements and the identification of the lines in the solar spectrum, which it will take a long time to work up, ready for publication. Hence, I have thought that a short account of what has been done up to the present time might be of interest to workers in the subject. In the prosecution of the work financial assistance has been received from the Rumford Fund of the American Academy of Arts and Sciences, as well as from the fund given by Miss Bruce to the Harvard Astronomical Observatory for the promotion of research in astronomical physics, and the advanced state of the work is due to such assistance.

The work may be summed up under the following heads:—

1. The spectra of all known elements, with the exception of a few gaseous ones, or those too rare to be yet obtained, have been photographed in connection with the solar spectrum, from the extreme ultra violet down to the D line, and eye observations have been made on many to the limit of the solar spectrum.

2. A measuring engine has been constructed with a screw to fit the above photographs, which, being taken with the concave grating, are all normal spectra and to the same scale. This engine measures wave-lengths direct, so that no multiplication is necessary, but only a slight correction to get figures correct to $\frac{1}{100}$ of a division of Angstrom.

3. A table of standard wave-lengths of the impurities in the carbons, extending to wave-length 2000, has been constructed to measure wave-lengths beyond the limits of the solar spectrum.

4. Maps of the spectra of some of the elements have been drawn on a large scale ready for publication.

5. The greater part of the lines in the map of the solar spectrum have been identified and the substance producing them noted.

6. The following rough table of the solar elements has been constructed entirely according to my own observations, although, of course, most of them have been given by others.

I do not know which are the new ones, but call attention to Silicon, Vanadium, Scandium, Yttrium, Zirconium, Glucium, Germanium, and Erbium, as being possibly new.

Silicon has lines on my map at wave lengths 3905.7, 4103.1, 5708.7, 5772.3, and 5948.7. That at 3905.7 is the largest and most certain. That at 4103.1 is also claimed by Manganese.

These tables are to be accepted as preliminary only, especially the order in the first portion. However, being made with such a powerful instrument and with such care in the determination of impurities, they must still have a weight superior to most others published.

The substances under the head of "Not in the Solar Spectrum" are often placed there because the elements have few strong lines or none at all in the limit of the solar spectrum when the arc spectrum, which I have used, is employed. Thus boron has only two strong lines at 2497. Again, the lines of bismuth are all compound and so too diffuse to appear in the solar spectrum. Indeed, some good reason generally appears for their absence from

Elements in the Sun, Arranged According to the Intensity and the Number of Lines in the Solar Spectrum.

According to Intensity.

Calcium.
Iron.
Hydrogen.
Sodium.
Nickel.
Magnesium.
Cobalt.
Silicon.
Aluminium.
Titanium.
Chromium.
Manganese.
Strontium.
Vanadium.
Barium.
Carbon.
Scandium.
Yttrium.
Zirconium.
Molybdenum.
Lanthanum.
Niobium.
Palladium.
Neodymium.
Copper.
Zinc.
Cadmium.
Cerium.
Glucium.
Germanium.
Rhodium.
Silver.
Tin.
Lead.
Erbium.
Potassium.

According to Number.

Iron (2000 or more).
Nickel.
Titanium.
Manganese.
Chromium.
Cobalt.
Carbon (200 or more).
Vanadium.
Zirconium.
Cerium.
Calcium (75 or more).
Scandium.
Neodymium.
Lanthanum.
Yttrium.
Niobium.
Molybdenum.
Palladium.
Magnesium (20 or more).
Sodium (11).
Silicon.
Strontium.
Barium.
Aluminium (4).
Cadmium.
Rhodium.
Erbium.
Zinc.
Copper (2).
Silver (2).
Glucium (2).
Germanium.
Tin.
Lead (1).
Potassium (1).

Doubtful Elements.

Iridium.	Ruthenium.	Tungsten.
Osmium.	Tantalum.	Uranium.
Platinum.	Thorium.	

Not in Solar Spectrum.

Antimony.	Cæsium.	Rubidium.
Arsenic.	Gold.	Selenium.
Bismuth.	Indium.	Sulphur.
Boron.	Mercury.	Thallium.
Nitrogen (vacuum tube).	Phosphorus.	Praseodymium.

Substances not yet Tried.

Bromine.	Oxygen.	Holmium.
Chlorine.	Tellurium.	Thulium.
Iodine.	Gallium.	Terbium, &c.
Fluorine.		

the solar spectrum. Of course, this is little evidence of their absence from the sun itself.

Indeed, were the whole earth heated to the temperature of the sun, its spectrum would probably resemble that of the sun very closely.

With the high dispersion here used the "basic lines" of Lockyer are widely broken up and cease to exist. Indeed, it would be difficult to prove anything except accidental coincidences among the lines of the different elements. Accurate investigation generally reveals some slight difference of wave-length or a common impurity.

Furthermore, the strength of the lines in the solar spectrum is generally very nearly the same as that in the electric arc, with only a few exceptions, as, for instance, calcium. The cases mentioned by Lockyer are generally those where he mistakes groups of lines for single lines, or even mistakes the character of the line entirely. Alto-

* Johns Hopkins University Circulars, Vol. x., No. 85.

gether there seems to be very little evidence of the breaking up of the elements in the sun as far as my experiments go.

Even after comparing the solar spectrum with all known elements, there are still many important lines not accounted for. Some of these I have accounted for by silicon, and there are probably many more. Of all known substances this is the most difficult to bring out the lines in the visible spectrum, although it has a fine ultra violet one. Possibly iron may account for many more, and all the elements at a higher temperature might develop more.

Then, again, very rare elements, like scandium, vanadium, &c., when they have a strong spectrum, may cause strong solar lines, and thus we may look for new and even rare elements to account for very many more. Indeed, I find many lines accounted for by the rare elements in gadolinite, samarskite, and fergusonite other than yttrium, erbium, scandium, praseodymium, neodymium, lanthanum, and cerium, which I cannot identify yet, and which may be without a name. For this reason, and to discover rare elements, I intend finally to try unknown minerals, as my process gives me an easy method of detecting any new substance or analysing minerals, however many elements they may contain.

The research is much indebted to the faithful and careful work of Mr. L. E. Jewell, who has acted as my assistant for several years. Preliminary publications of results will be made in the *Johns Hopkins University Circulars*.

Among the latest results I may mention the spectroscopic separation of yttrium into three components, and the actual separation into two.

RESEARCHES ON "OIL FOR REDS" (ALIZARIN OIL).

By M. SCHEURER-KESTNER.

THE sulphonic compound which is found in "oil for reds" may be isolated by treating this product with a suitable mixture of water and ether. The ether dissolves the fatty acids which are not sulphonised (or rather desulphonised by the action of water during the washing of the crude product obtained on allowing sulphuric acid to act upon castor oil), whilst the sulphonised substance remains in solution in the watery portion, separate from the ethereal stratum. To isolate it the aqueous solution is precipitated with a solution of sodium sulphate at 10° Baumé.

On evaporating the ethereal stratum we obtain the fatty acids, more or less polymerised, the weight of which may be determined, whilst the precipitation of the aqueous solution enables us to give account of the sulphonic body. In general two preparations made under conditions which seem identical do not always give the same results. The "oil for reds" obtained contains variable proportions of the two principal products. The fatty acids by the action of the water during the washings are thus changed to a greater or less extent, and the solubility of the oil in water is so much the greater as these desulphonised fatty acids are present in a smaller quantity. In fact, they are soluble only by reason of the presence of the sulphonised body, and they give the solution that fluorescence from which a solution of oil is never free.

As for the degree of polymerisation, it seems to be more considerable in the substances extracted by ether than in the soluble body. Thus the fatty acids withdrawn from one and the same preparation, and separated in the state of sulphonised and non-sulphonised bodies respectively, gave the molecular weights 402 and 472 (the molecular weight of the normal acid is 298).

Sulphoricinoleic acid, precipitated from its watery solution by sodium sulphate, forms a syrupy hydrate without any appearance of fluorescence when it has been freed from the non-sulphonised fatty acids by means of ethers.

It enters into the composition of the most soluble "oil for reds" to the extent of 40 to 50 per cent, the remaining 50 or 60 per cent being formed of fatty acids insoluble in water. In this calculation the accompanying water is disregarded.

The sulpho-fatty acid in an isolated state has a composition approaching that of diricinosulphonic acid.

It is impossible to dehydrate it completely without decomposing it into sulphuric acid and fatty acid. If it is dried at a temperature not exceeding 60° its decomposition is very slight, and it then contains 4 per cent of sulphur.

We may give account of the composition of oil for reds by using in succession litmus and phenolphthalein as indicators. The litmus turns blue as soon as the sulphonic compound is saturated, whilst the phenolphthalein only becomes coloured much later, and then only if the non-sulphonised fatty acid has been saturated. Upon these properties the author has founded an analytical process, which by means of two simple titrations made successively gives the proportion of the two principal elements of oils for reds. The difference between the two values found on making use of a standard solution of ammonia and the indication above mentioned, shows the quantity of ammonia which has served for the saturation of the desulphonised acids.

Care must be taken to use always the same quantities of water, otherwise the results will not be comparable. This experiment may also be useful from a practical point of view, since the author has proved that the tone of the clearing of alizarin colours depends exactly on the presence of a larger or smaller proportion of the sulphonised compound.

The standard found with litmus corresponds to the weight of the barium sulphate which oil for reds gives if its sodium salt has been ignited. It is also easy to follow the polymerisation of ricinoleic acid, measuring it by its capacity for saturation, and making use of phenolphthalein.

Normal ricinoleic acid, if treated with sulphuric acid as castor oil is done, gives a product like that of castor oil. On analysing it by means of double titration the author has found a sulphonised acid and polymerised fatty acids in the proportion of 60—65 to 100 of the former.

He proposes to show ultimately that ricinoleic acid is easily polymerised, not merely by the action of heat, but by that of steam, and that it may be restored to its normal state by the action of soda under certain conditions.—*Comptes Rendus*.

THE DETERMINATION OF NITRIC AND NITROUS ACIDS IN SPRING WATER.

By MAX ROSENFELD.

PYROGALLIC acid has not been duly appreciated as a reagent for nitric and nitrous acids. Many experiments have convinced the author that this reagent under certain conditions is not inferior to any other for the detection of nitric acid, and that it appears especially suited for the determination of the above acids in spring water.

For the determination of nitric acid we use a solution of 0.5—1 grm. pyrogalllic acid in 100 c.c. water.

For carrying out the reaction the author pours 3 c.c. of the water under examination into a test-glass tapering to the bottom, and adds 6 c.c. of strong sulphuric acid, which is poured in as rapidly as possible from a small test-tube, adding carefully a drop of the pyrogalllic acid solution. The upper stratum of the liquid takes at once or in the course of a few minutes (according to the proportion of nitric acid present) a violet to dark brown colour. It is advantageous, about two minutes after the addition of the pyrogalllic acid, to turn the liquid carefully round, so that the coloured stratum may occupy the space of about 6

c.c. For this purpose it is well to make a mark on the test-glass indicating the volume (3 c.c.) of the liquid used for the test. If 5 milligrammes nitric acid (N_2O_5) per litre be present the colour appears very distinctly after a few minutes; with 10 milligrammes nitric acid per litre a violet colour appears at once after shaking; with 15 milligrammes the upper stratum appears brown either at once or after a short time. In this manner 1 milligramme of nitric acid may be detected per litre. If there are less than 3 milligrammes nitric acid (N_2O_5) per litre the colour is perceptible only after a time, and must then be compared with the colour which appears under the same circumstances in pure, distilled water. In such a comparative determination not more than one small drop of the reagent must be used, because pure sulphuric acid is turned a light rose by larger quantities of pyrogallic acid. It is further necessary to diffuse the pyrogallic acid through the space above mentioned by careful shaking immediately after it has been added. The difference in the colour of both liquids is distinctly perceptible with a proportion of 1 milligramme nitric acid per litre, and consists herein, that in the nitric acid solution the coloured stratum becomes more intense downwards, and thus appears to have a sharply-marked boundary. In pure distilled water the colour becomes less intense below, and fades away gradually.

In carrying out the reaction it is absolutely necessary to mix the liquid to be tested with sulphuric acid exactly in the proportions here indicated. It occurs in presence of large quantities of nitric acid that the dark colour which first appears disappears again on shaking. In such a case several drops of the pyrogallic acid must be added to the solution.

As the difference of intensity in the colour produced by pyrogallic acid according to the quantity of the nitric acid present, may be distinctly recognised (up to the proportion of 15 milligrammes per litre), and admits of a comparison with the tones of colour obtained in the same conditions in solutions containing a known amount of nitric acid, this method may serve for an estimation of the nitric acid in spring water.

If this estimation is only rough it allows us to decide very rapidly whether a potable water contains more or less than the permissible maximum of nitric acid.

The test-glasses in which the operation is performed must not be previously wiped out with linen or cotton cloths, since even small quantities of cellulose in contact with sulphuric acid produce the colouration of pyrogallic acid.

The author has examined the sensitiveness of Schöenbein's reaction, and finds that there may be founded upon it a comparative colorimetric method for the estimation of small quantities of nitric acid.

The reagent is a solution of 0.5 grm. pyrogallic acid in 90 c.c. of water, to which are added 10 c.c. of concentrated sulphuric acid.

In order to perform the reaction 100 c.c. of the water in question are placed in a narrow cylinder of colourless glass, 18–20 c.m. in height, and mixed with 2 c.c. solution of pyrogallic acid. If the liquid contains 0.4 m.grm. nitrous acid (N_2O_3) per litre, the yellow colour appears immediately; with 0.3 m.grm. in six minutes; with 0.2 in about twenty-three minutes; whilst with 0.1 m.grm. nitrous acid per litre the colour appears only after the lapse of about seven hours. The difference in the colour is perceptible with a difference of 0.005 m.grm. nitrous acid in 100 c.c. of water if this quantity does not contain more than 0.05 m.grm. nitrous acid. With larger proportions the colour, if seen from above through the column of liquid, is too intense to allow of the difference of colouration being distinguished. Within the above limits (0.01–0.05 m.grm. nitrous acid in 100 c.c. of liquid) the differences of colour remain perceptible, so that the limit of error per litre is less than 0.1 m.grm. Pyrogallic acid is also turned yellow by free alkalis.—*Zeitschrift Anal. Chem.*, vol. xxix., p. 661.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

March 5th, 1891.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

MR. A. W. OXFORD was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. William Bate, National Explosives Company, Hayle, Cornwall; Alexander Lauder, University College, Bangor, North Wales; Cecil George Freer Thonger, Colonial College, Hollesley Bay, Suffolk.

The following papers were read:—

14. "*Crystalline Form of the Calcium Salt of Optically Active Glyceric Acid.*" By ALFRED E. TUTTON, Royal College of Science, London.

This paper presents the results of a complete crystallographical investigation of the calcium salt, $\text{Ca}(\text{C}_3\text{H}_5\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, of the optically active (dextrorotatory) form of glyceric acid described (*Trans.*, 1891, p. 96) by Frankland and Frew. The crystals belong to the monoclinic system, and are hemihedral, the forms $\{111\}$ and $\{011\}$ being only developed at the right-hand extremity of the symmetry axis, and the forms $\{1\bar{1}1\}$ and $\{2\bar{1}1\}$ at the left extremity. The hemihedrism is also manifested by a difference in the prism faces of the form $\{110\}$, those upon the right side of the symmetry plane being much more brilliant than those upon the left side. The ratio of the axes is $a:b:c = 1.4469:1.06694$. A complete table of angles is given, the result of the measurement of a dozen crystals. The optic axial plane is perpendicular to the symmetry plane, and the first median line is nearly perpendicular to the basal plane. The true angle of the optic axes is $2V_{\text{Li}} = 34^\circ 56'$, $2V_{\text{Na}} = 35^\circ 28'$, $2V_{\text{K}} = 36^\circ 16'$. The mean refractive index β is 1.4496, 1.4521, and 1.4545 for lithium, sodium, and thallium light respectively. The sign of double refraction is positive. The calcium salt of this dextrorotatory glyceric acid must therefore be added to the list of optically active substances whose crystals are also hemihedral, a list which includes all the hitherto well investigated cases.

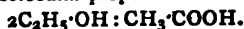
15. "*Fermentations Induced by the Pneumococcus of Friedländer.*" By PERCY F. FRANKLAND, Ph.D., B.Sc., (London), ARTHUR STANLEY, and WM. FREW.

That this well known micro organism is capable of inducing fermentative changes in suitable solutions of glucose and cane-sugar was first pointed out by Brieger, *Zeit. f. Physiol. Chem.*, vol. viii., p. 306–331, and vol. ix., 1–7. The authors have confirmed these observations of Brieger's, and have further found that the organism ferments maltose, milk-sugar, raffinose, dextrin, and mannitol, but that, like the *Bacillus ethaceticus*, it does not attack dulcitol. They have made a special study of the fermentations of glucose and mannitol, determining quantitatively the proportions in which the several products are formed. These products are in each case ethyl alcohol, acetic acid, generally accompanied by a little formic acid and a trace of succinic acid, carbon dioxide, and hydrogen. Both the glucose and mannitol were in all cases only partially fermented, and the decomposition of the glucose was especially incomplete, glucose being apparently less readily attacked by the organism than mannitol and cane-sugar. The fermentation was not rendered more complete by furnishing the organism with a more abundant supply of nitrogenous food.

In the first instance, fermentations were conducted on 60 grms. of glucose and mannitol respectively, with the following results:—

	I. Grms. glucose.	I. Grms. mannitol.	III. Grms. mannitol.
Ethyl alcohol	0.5897	4.11	5.06
Volatiles acids calcu- lated as acetic acid	1.6578	2.9921	3.1617

The products of the mannitol fermentations are not only qualitatively similar to those obtained in the fermentation of the same substance by the *Bacillus ethaceticus*, but the relative proportions in which they are formed are almost identical, the ratio corresponding closely to the molecular proportions



In the subsequent experiments, in which the volume and composition of the evolved gases were determined, only 12 grms. of mannitol were employed; in this case also very similar ratios were obtained, although a period of two years had elapsed since the above fermentation had been carried on.

The following results of analysis show the composition of the gas evolved in a fermentation with 12 grms. mannitol, after the air in the apparatus had been displaced:—

	16th day.	23rd day.	34th day.	41st day.	Average.
CO ₂ ..	51.77	61.29	66.18	65.47	61.18
O ₂ ..	0.09	0.15	0.22	0.09	0.14
H ₂ ..	47.97	38.26	33.47	34.19	38.47
N ₂ ..	0.17	0.30	1.13	0.25	0.21
	100.00	100.00	100.00	100.00	100.00

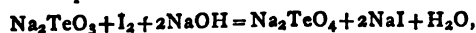
The lower proportion of carbon dioxide in the earlier part of the fermentation is doubtless due to the liquid saturating itself with the gas, and the excess at the end to the slow decomposition of the calcium bicarbonate formed in the first instance. The average composition of the gas may be taken to be 6 volumes or molecules of carbon dioxide to 4 volumes or molecules of hydrogen. Taking into account the actual volume of gas given off, the several products are in very close accord with the molecular proportions; $9C_2H_6O : 4C_2H_4O_2 : 12CO_2 : 8H_2$, derived from 6 mol. props. of mannitol, 2 mol. props. of carbon dioxide being formed by the action of the acetic acid on the added calcium carbonate.

By plotting out the volumes of evolved gas on a diagram, in which the ordinates represent the volumes in cubic centimetres, and the abscissæ the time of fermentation in days from the date of inoculation, the authors obtain a curve for which the equation is—

$$v = \frac{6.731^x}{1 - 0.0061x + 0.005741^x}.$$

16. "The Volumetric Estimation of Tellurium. Part II." By B. BRAUNER, Ph.D.

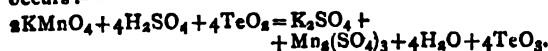
The author finds that although a solution of iodide in potassium iodide acts on alkaline tellurates in accordance with the equation



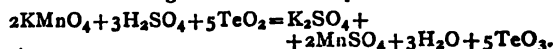
the action is very slow and incomplete at the ordinary temperature, so that heat must be applied for its completion. On acidification the excess of iodine is set free, but it has hitherto been found impossible to exactly determine the end of reaction by titration with thio-sulphate.

The titration of solutions of tellurium dioxide in chlorhydric acid with permanganate is found to be impracticable, as varying quantities of chlorine are evolved during the process.

When a solution of tellurium dioxide in sulphuric acid is titrated with permanganate, the following interchange occurs:—



In order to destroy the manganic salt which is formed, either decinormal ferrous sulphate or oxalic acid is added until decolorisation takes place, after which permanganate is added in slight excess. After subtracting the volume of permanganate corresponding to the ferrous salt or to oxalic acid from the total of permanganate added, the quantity of tellurium dioxide is calculated from the volume of permanganate necessary for its oxidation, as if the following action had taken place:—



Owing to the evolution of some oxygen, the quantity of tellurium dioxide found is greater by 1 per cent than that calculated from the equation.

In alkaline solution the change which takes place is that indicated by the equation



After addition of an excess of sulphuric acid oxalic acid is used for re-titration in the manner previously stated, but the results are 0.35 per cent too high. The results obtained by both methods are accurate when the corrections mentioned are applied.

17. "Chloro- and Bromo-derivatives of Naphthol and Naphthylamine." By HENRY E. ARMSTRONG and E. C. ROSSITER.

This communication is a continuation of one published in the *Proc. Chem. Soc.* in 1889.

1 : 4-Dichloro- β -naphthol.—A better yield of this compound than is obtained by Zincke's method appears to result from the gradual interaction of chloro- β -naphthol and sulphuryl chloride at ordinary temperatures, about 30 per cent of the chloro- being converted into the dichloro-compound. The mixture obtained on steam-distilling the crude product is sulphonated, and the mixture of salts resulting from the direct neutralisation of the acid solution with potassium carbonate is extracted with boiling alcohol, which dissolves the dichloro- but not the monochloro-sulphonate. The dichloronaphthol is recovered by heating the sulphonate with dilute sulphuric acid at 210°.

1 : 4 : 4'-Trichloro- β -naphthol.—The oily by-product obtained in preparing a large quantity of trichloro- β -ketonenaphthalene, when allowed to stand during many months, was found to slowly give off hydrogen chloride and to become partially solid; the solid was freed from oil by washing with acetic acid and was re-crystallised from this solvent. The substance thus obtained proved to be a trichloro- β -naphthol, and as it yields 1 : 2 : 3-chlorophthalic acid on oxidation, and is reduced by sodium amalgam to 1 : 4-dichloro- β -naphthol, it is most probably the 1 : 4 : 4'-modification. It crystallises in short soft needles melting at 157–158°; its acetyl derivative melts at 129°.

Chloro- β -naphtholsulphonic Acid.—1-Chloro-, 1 : 3-, and 1 : 4-dichloro-, and 1 : 3 : 4'- and 1 : 4 : 4'-trichloro- β -naphthol are all sulphonated with the greatest care, each yielding a derivative of 1 : 3'-(Schaefer's) β -naphtholsulphonic acid, proof that this is the case being afforded by the formation of this acid from each of the chloro-acids on reduction. This result is noteworthy inasmuch as 3' : 1-dibromo- and bromochloro- β -naphthol—in which the position occupied by the sulfo-group in Schaefer's acid is occupied by bromine—are distinctly less readily sulphonated than any of the chloronaphthols referred to; and it is a matter of interest also that neither is a derivative of the Weinburg β -acid, isomeric with Schaefer's formed from them; hence it would seem that a β -sulphonic acid only results when the β -3'-position is free, viz., that which is symmetrically situated relatively to the β -OH group.

1 : 3'-Dibromo and Bromochloro- β -naphthol.—In the previous communication it was stated, that on brominating either bromo- or chloro- β -naphthol, the bromine is introduced into the second nucleus. To determine the position taken up by the bromine, the bromochloronaphthol was

distilled with PCl_5 ; 1:2:3'-trichloronaphthalene was one of the products obtained, and it would seem therefore that it occupies the position 3'. As both dibromo- and bromochloronaphthol afford 1:3:4-bromophthalic acid on oxidation, this conclusion may be regarded as established. Independent confirmation of this result is afforded by the observation that chloro- β -acenaphthylide is converted by bromine almost quantitatively into a bromochloracenaphthalide (m.p. 216°), which affords a bromochloronaphthylamine (m.p. 119°) and a bromochloronaphthalene (m.p. 60°) in which the bromine atom occupies the β -3'-position; also by Claus's recent statement that when brominated bromo- β -acenaphthalide in like manner yields 1:3'-dibromo- β -naphthylamine (*J. pr. Chem.*).

The conclusion thus arrived at, however, is in opposition to that to be deduced from Smith and Meldola's statement, that tetrabromo- β -naphthol, when oxidised, yields the bromophthalic acid whose anhydride melts at 134° , i.e., the 1:2:3-acid. The authors have, therefore, studied the action of bromine in excess on β -naphthol. They find that, contrary to Smith's statement, the preparation of tetrabromonaphthol is attended with very considerable difficulty, the product chiefly consisting of tribromonaphthol; the separation of this latter by crystallisation is difficult, but is easily accomplished by acetylating the crude product and re-crystallising the acetate from benzene and from acetic acid. The acetate crystallises in long fine needles melting at 184° , and is very easily hydrolysed. Tribromonaphthol melts at 155 – 156° ; on oxidation with alkaline permanganate it yields 1:3:4-bromophthalic acid. The authors are still engaged in investigating this compound and the other products of the action of bromine in excess on β -naphthol.

Action of Nitric Acid and of Oxidising Agents on Chloro- and Bromo-naphthols.—Nearly all the chloro- and bromo-derivatives of β -naphthol yield characteristic quinone derivatives when submitted to the action of nitric acid; in most cases the formation of these is preceded by that of an unstable intermediate compound, the determination of whose composition presents great difficulties. The final product of the action of nitric acid is phthalic acid. Alkaline permanganate is not always a suitable agent to employ if the object be to completely oxidise the naphthol; thus the main product of its action on dibromo- β -naphthol, for example, is the acid—



which, on distillation, yields bromophthalide.

Anniversary Meeting.

Wednesday, March 25th, at 8 p.m.

THE CHEMICAL SOCIETY. JUBILEE MEETING.

A MEETING in celebration of the Jubilee of the Society was held in the Theatre of the London University on Tuesday, the 24th February, 1891, Dr. Russell (the President) being in the Chair, and a numerous audience of Fellows and visitors being present.

The proceedings were opened by the following address from the President:—

We meet to-day to celebrate the fifty years' existence of our Society, a time, if measured by the progress which our science has made, equal to centuries of former ages, but which in years is so brief a space that we have, I am happy to say, with us to-day some of those who were present and who took an active part in the foundation of the Society, and I need hardly say with how much interest we shall listen to their reminiscences of the time and circumstances connected with the birth of our Society.

I would, by way of introduction, say a few words, first, with regard to our Society, and afterwards with regard to the state of chemistry in England when our Society was founded. We boast, and I believe rightly, that our Society holds the distinguished position of being the first which was formed solely for the study of chemistry. Chemistry and physics, twin sisters, had hitherto always dwelt together, and many were the societies, both in this country and abroad, devoted to their joint study and development.

In London there was the Royal Society, which had hitherto received the most important chemical papers; there was also the Society of Arts, which is 110 years, and the British Association, which is ten years senior of our Society. In Manchester the Literary and Philosophical Society had been founded and actively at work since 1781; and we admit that our neighbours at Burlington House, the Astronomical, Antiquarian, Linnean, and Geological Societies are all our seniors: they had a distinct individuality and literature of their own, which called them into existence some forty to eighty years before the commencement of our Society. Small private chemical societies, no doubt, existed; they are the natural fore-runners of a large society, and become merged into it. The Chemical Section of the British Association, which is an ephemeral and peripatetic Chemical Society, had existed from the founding of that body. If we turn to other countries we find that, much as our science had been cultivated on the Continent, it did not, until later times, engross a whole society to itself, the French Chemical Society not having been formed until 1857, and the now great Berlin Chemical Society not until 1868. Our interest, however, at the moment is rather in the growth of chemistry in this country than in what occurred elsewhere.

To-day we may learn how it came about that the first Chemical Society was established in England. I may, however, state that the reason for our meeting depends on the official record that on the 23rd of February, 1841, twenty-five gentlemen "interested in the prosecution of Chemistry" met together at the Society of Arts to consider whether it be expedient to form a Chemical Society. Of the twenty-five who then met I am happy to say three are present—Sir W. Grove, Sir L. Playfair and Mr. Heisch, and Dr. Longstaff and Mr. J. Cock are others of this band who are still alive but not present.

These twenty-five gentlemen appear without dissent to have come to the conclusion that it was expedient to form a Chemical Society, and appointed a committee of fourteen to carry this resolution into effect. So expeditious were they in their work, that in little more than a month the first general meeting was held, and the provisional committee brought forward a report embodying a plan for the constitution and government of the Society, and this plan remains essentially the same, save in one point, to the present day. I refer to the formation of a museum of chemical specimens; this project was abandoned some years ago. It is worth recording that at this first general meeting Thomas Graham was elected President; W. T. Brande, Esq., J. T. Cooper, Esq., J. F. Daniell, Esq., R. Phillips, Vice-Presidents; Arthur Aikin, Esq., Treasurer; Robert Warington, Esq., E. F. Tschermacher, Esq., Secretaries; Council—Dr. T. Clark, Rev. J. Cumming, M.A., Dr. C. Daubeny, T. Everitt, Esq., T. Griffiths, Esq., W. R. Grove, Esq., H. Hennell, Esq., G. Lowe, Esq., W. H. Miller, Esq., M.A., W. H. Pepsy, Esq., R. Porret, Esq., Dr. G. O. Rees. Also that the Society then numbered seventy-seven members. We hail Sir W. Grove as being the most active member who is still among us in founding our Society, for he was a member of the first council, was present at the first meeting, and was a member of the provisional committee. I must here add to the official record, for it does not tell us how these twenty-five gentlemen "interested in the prosecution of chemistry" were collected together at one

time and place. Obviously, some special force was required to build up this complicated molecule; that special force was embodied in and exercised by Robert Warington. By his activity and energy he brought about this meeting, and we can imagine how difficult and troublesome a work it probably was, how some of these gentlemen had to be instigated to action, others repressed, some convinced that the aim was desirable, others that it was feasible. But whatever the difficulties were Mr. Warington succeeded, and to him we are indebted for the formation of our Society. Although he has passed away, he is ably represented here to-day by his son. The love for the Chemical Society has proved to be hereditary: Mr. Warington of to-day is a most active and valued member; is one of our Vice-Presidents; and, as our programme shows, is about to present to us records connected with the early history of our Society which are of great interest now and will become of increasing value as time goes on.

I turn now at once from these matters immediately connected with our Society to the consideration of what was being done in chemistry in this country fifty years ago. At that time public laboratories for the systematic teaching of chemistry did not exist in London. The number of real students of chemistry in this country was very small. They were looked upon by their friends as being eccentric young men, who probably would never do any good for themselves, and these few students found practical instruction in the private laboratories of some of the London teachers.

The practical teaching of chemistry appears to have been undertaken in Scotland much earlier than in England, for Dr. D. B. Reid held practical classes at the University of Edinburgh as early as 1832. Graham came to London from Glasgow in 1837, and until the opening of the Birkbeck Laboratory in 1846, he had from time to time private students working in his laboratory. And so with the other teachers, who all had private or articulated pupils. I doubt whether the pupils received much systematic instruction, but they gained an insight into laboratory work, saw how apparatus was put together, and how analyses were made. We have, indeed, to wait some years before public laboratories are established, for not until 1845 is the College of Chemistry opened, and this appears to have been really the first first public laboratory in London, and its object, as stated by its founders, is "to establish a practical School of Chemistry in England." About the same time both University and King's College establish laboratories. The Council of our Society recognised the importance of these occurrences, for in the Annual Report in 1847 we read, although an event not immediately connected with the Society, the Council has much pleasure in commemorating the late successful establishment in London of chemical laboratories, expressly designed to further the prosecution of original research. The new laboratories of the College of Chemistry, and of the two older Colleges of the London University, now offer facilities for practical instruction and research not surpassed, we believe, in any foreign school.

While speaking of laboratories in London, I should, however, mention that the Pharmaceutical Society established a laboratory especially, if not exclusively, for its own students as early as 1843.

It was not till several years later—till 1850 and 1851—that the medical schools in London established classes of practical chemistry.

If we consult the scientific journals of the time immediately preceding the formation of our Society, we find it was by no means a time of chemical activity in this country, but was rather a dull time, given more to the study and slow development of the science than to discovery. Methods of analysis, both organic and inorganic, had been much improved, and the dominant idea was the determination of the empirical composition of bodies, and the preparation of new compounds, whose existence was predicted by a study of Dalton's Atomic Theory. Graham,

Kane, and Johnson, of Durham, were the leaders in scientific chemistry, and the authors of the most important chemical papers of the time. Graham had very lately published his notable paper on the constitution of salts—a paper which gained for him, some years after its publication, a Royal medal. Kane was an active worker and bold theorist, and at this time his reputation was much increased by a paper on the Chemical History of Archil and Litmus. Johnson was also a most active chemist. His contributions relate to many branches of the science, but especially to the chemical composition of minerals. In 1841, however, he is engaged on a long series of papers on the constitution of resins. He will probably be best known and remembered as an agricultural chemist. Faraday we can hardly claim as a chemist at this time, for he was then rapidly publishing his long series of Experimental Researches in Electricity. While speaking of electricity I should state that it was in 1840 that Smee described his battery, and the Society of Arts awarded him a gold medal for it. An important branch of our science was, however, coming into existence—a branch which has found many and successful investigators in this country; I mean photography. It was in 1840 that Herschel published in the *Philosophical Transactions* his elaborate paper on the chemical action of the rays of the solar spectrum, a paper in which he recognises a new prismatic colour beyond the violet, and chemical activity in the spectrum beyond the red, and besides discussing many other matters, establishes his previously discovered hyposulphite of soda as the best agent for the fixing of sun pictures. Fox-Talbot had previously given an account of Photogenic drawing, and claims that as far back as 1835 he took pictures of his house by means of a camera and chloride of silver paper, but it is not till 1838 that the Secretary of the Royal Society extracts from him a clear account of the details of his process, and it is in 1841 that he is granted a patent for improvements in obtaining pictures or representations of objects. Again, in the following year, Herschel publishes another paper of much importance. I can here only mention how actively this line of research was prosecuted by Robert Hunt, how many ingenious and interesting experiments he made, and how valuable was the account he afterwards gave of this subject in his "Researches on Light." Thus the work done in this branch of chemistry at the time of which I am speaking is certainly noteworthy, probably more so than in other branches of chemistry. In fact, of other advances in chemistry there is little to record, but I may mention that Clarke's process for determining the hardness of water also holds its jubilee this year, for it was in 1841 that a patent was granted to Dr. T. Clarke for a new mode of rendering certain waters less impure and less hard.

Not a single chemical paper appears in the *Phil. Trans.* for 1841, but there are two papers which were much discussed at this time, and although they were readily shown to be erroneous, still are interesting as indicating the chemical ideas of the day. One is by Robert Rigg, who is carrying on an experimental inquiry on Fermentation, being termed "Additional Experiments on the Formation of Alkaline and Earthy Bodies by Chemical Action when Carbonic Acid is Present"; it is published in the *Proceedings of the Royal Society*. The other is a paper by Dr. S. M. Brown entitled "The Conversion of Carbon into Silicon," published in the *Transactions of the Royal Society of Edinburgh*.

With regard to the first paper, Mr. Rigg believes that he has demonstrated that when fermentation takes place, a great and direct increase in alkaline and earthy salts, viz., of potash, soda, and lime occurs, an increase varying from 15 to 19 times the original amount. Denham Smith, who has only very lately passed away, showed that the theory simply rested on inaccurate experiment.

The object of the other paper is to demonstrate that on heating paracyanogen, nitrogen is given off, and a residue of silicon remained. Dr. Brett and Mr. Denham Smith

controverted this, and in a paper in the *Phil. Mag.* proved that the supposed silicon was simply carbon in a very incombustible state. So important an experiment was this alleged conversion of carbon into silicon considered to be at the time of its publication, that it attracted Liebig's attention, and in a letter to Dr. Playfair, which was communicated to the meeting of the British Association at Plymouth in 1841, Liebig says, he has repeated Dr. Brown's experiment on the production of silicon from paracyanogen, but has not been able to confirm one of his results.

As far as pure chemistry is concerned it was rather a time of repose. The beginning of the century had been a brilliant time for chemistry in England. Dalton had published his atomic theory; Davy had decomposed potash and soda, and had demonstrated that chlorine was an element; and Cavendish and Wollaston were then still at work. In fact, the most important discoveries of that time were made in this country, but I fancy that during this later period a feeling grew up that the age of brilliant discoveries was over, and that apart from the preparation of a few new compounds, the essential work of the time was analysis, and the determination of the percentage composition of bodies. Still, much quiet study of the science was going on, as is indicated by the considerable demand which existed for good text-books. Henry's, Turner's, Kane's, and Graham's Chemistry—all these, without mentioning others, went through numerous editions, and played a very important part in the spread of chemical knowledge in our country.

Another text-book, which is interesting as showing how little organic chemistry was studied in this country, is Dr. Thomas Thompson's work on "Vegetable Chemistry." Dr. Thompson states in his preface that the object of the book is to lay before the British public a pretty full view of the present state of the chemistry of vegetable bodies, and further he says, "that the ultimate analyses he gives have, with very few exceptions, been made upon the Continent, and principally in Germany and France. British chemists have hardly entered on the investigation." Evidently, then, at this time organic chemistry had been but little studied in this country.

When our Society was founded, Thomas Graham was certainly the most distinguished chemist in England. He came to London in 1837 as professor of chemistry at University College, succeeding Edward Turner. The work he had already accomplished was of a high order, and he was now occupied in writing his book which appeared in 1842.

The book was an admirable account of the chemistry of the time; it contained a well-arranged and clearly written introduction, describing the principles and latest discoveries in those branches of physics which bear most directly on chemistry. There was also an able and succinct account—probably the best which had then appeared in this country—of organic chemistry; and with regard to physiological chemistry, he states in the preface that he gives a "condensed view of the new discoveries in this department, which now enters for the first time into a systematic work on chemistry."

There are, however, indications that a knowledge of the discoveries and discussions going on the Continent only slowly reached this country. This is strongly insisted on in the *Phil. Mag.* of 1841, by Messrs. Francis and Croft, who state that "but little of what is done abroad, especially in Germany, seems to find its way into England, or at least until the lapse of some years." In proof of this statement they mention results lately published by Dr. Apjohn, Prof. Johnston, and Dr. Golding Bird, all of which had been known on the Continent some time previously. A valuable series of communications described as "Notes of the Labours of Continental Chemists," is afterwards communicated by these chemists to the *Phil. Mag.*, and continued for several years.

The visit of Liebig in 1837, when he attended the meeting of the British Association at Liverpool, must

have given some stimulus to the study of organic chemistry in England, and we find that he undertook to report to the British Association on "Isomeric bodies," and also on organic chemistry, and this great undertaking resulted in his two works, the one "Chemistry, in its Application to Agriculture and Physiology," and the other, "Chemistry, in its Applications to Physiology and Pathology." Both books were dedicated to the British Association, the first appearing in 1840, the second in 1842. It is very difficult for us now to realise the importance of these works, and properly to appreciate not only the large amount of new knowledge which they contained, but, what is of still greater importance, the novelty of treating such subjects in a truly scientific spirit. Gradually this treatment of the subjects became understood and appreciated, and people took a higher view of chemistry, and regarded it as a true science, and not merely as a study which might lead to useful results.

If, then, it be true that chemistry at this epoch was not rapidly progressing in this country, we naturally ask how it came about that our Society from its very foundation was so successful. The explanation is not difficult to find, nor doubtful, for we have only to turn from our own country to the Continent and learn what is happening there. Liebig is at Giessen, Wöhler at Göttingen, Bunsen at Marburg, Dumas, Laurent, Gerhardt, and a host of distinguished and active chemists in France, and at this time even Berzelius and Gay-Lussac are alive. Liebig, with his wonderful energy and ability, was powerfully advocating the theory of compound radicals, and was extending in every direction our knowledge of organic chemistry, and inspiring all who came within the range of his influence with a love for investigation. Dumas, at the same time, both as a chemist and a finished advocate, was advancing his views on substitution and chemical types. Laurent, and afterwards Gerhardt, were, with conspicuous ability, showing how these theories were to be extended and modified so as to assume a form which has even with the lapse of time been but little altered. Thus on the Continent it was a time of wonderful activity; chemistry was every day becoming more of a true science, and the constitution as well as the composition of bodies was actively being discussed and investigated. This activity on the Continent took time to reach and really affect us here. The older chemists thought the new theories were visionary and unsound, the simple theories of their younger days were being swept away, and only slowly did they realise the meaning of the newer form of their science; but the wave of progress could not be stopped, and in this country we had been ripening for the change. Clearly the immediate cause of this sudden increase of chemical activity in England was Liebig. His famous school had now been established for several years at Giessen, and if the older men in this country did not altogether put their trust in him, the younger men, breaking through all restraint, flocked from this country to his laboratory, there to become indoctrinated with his enthusiasm for the study of chemistry, and to learn how scientific investigation was to be carried on. At this epoch our Society was founded, and our Journal shows how successful Liebig's teaching was, how a new spirit was instilled into English chemistry, and how much valuable work his students did. Our Society gave them a ready means of publishing their discoveries, and a meeting place for discussion and mutual interchange of ideas. Thus do I explain the success which from the first has attended on our Society; and having now led you to this point I stop, for my part was merely to speak the prologue, and I leave the story of the development of our Society in other hands.

A Gas-Balance with a Compensator.—A. Sievert and W. Durr.—This apparatus differs from that of Lux by the circumstance that the hollow sphere suspended to the weigh-beam is essentially closed and filled with air.—*Zeit. f. Anal. Chem.*, Vol. xxix, Part 4.

PHYSICAL SOCIETY.

March 6th, 1891.

Prof. W. E. AYRTON, F.R.S., President, in the chair.

Mr. H. A. MIERS, M.A., and Mr. W. Lucas, M.A., were elected Members of the Society.

Mr. JAMES SWINBURNE read a "Note on Electrostatic Wattmeters."

After referring to the history of the electrometer method of measuring power developed by alternating currents, the author pointed out that the necessity for taking two readings from which to determine the watts might be obviated by having the quadrants separate instead of connected in pairs as in the ordinary method. Non-inductive resistances are connected to the transformer, motor, or other apparatus in which the power is to be measured, so as to be in series with the apparatus, and on opposite sides of it; and the four ends of these two resistances are connected with the four quadrants. Under these circumstances the deflection of the needle is a measure of the watts. To increase the maximum deflection obtainable so as to make an instrument capable of being read by a pointer, the needle is made in two halves, fixed one below the other on the same stem, and, instead of quadrants, semicircular boxes are employed. In this way a range of 130 degrees is obtainable.

Prof. PERRY enquired as to what kind of law the instrument had, and Mr. BLAKESLEY asked whether it was convenient to use.

Mr. E. W. SMITH pointed out that there was no necessity to take two observations in the ordinary electrometer method, for, by using a false zero, one deflection gave the watts. Further, the use of the false zero rendered it unnecessary to employ any other voltmeter when experimenting at constant pressure.

The PRESIDENT said the historical part of the paper was not quite correct, and recalled attention to the fact that when high pressures were used a single reading obtained with the ordinary method of counting up gave the power. For ordinary low voltages, however, the false zero method described by Mr. Smith was very convenient.

Mr. SWINBURNE, in reply to Mr. Smith, said the observation of the false zero really meant another reading. As to the law of his wattmeter, referred to by Prof. Perry and the President, he said he never calculated a law, but calibrated the instruments directly.

Prof. S. P. THOMPSON, D.Sc., now took the chair, and a paper on "Interference with Alternating Currents," by Prof. W. E. AYRTON, F.R.S., and Dr. SUMPNER, was read by the latter.

The paper relates to the phenomena which occur when alternating electric pressures are impressed on circuits made up of various combinations of resistances, condensers, arcs, and inductive coils; to the characteristics of alternators; to the properties of transformers; and to the peculiarities exhibited by the Ferranti mains.

In one of the experiments an inductive coil and a condenser were connected in series, and a pressure of 25 volts as measured by a Cardew voltmeter, impressed on its terminals; the pressure on the two parts, measured in the same way, were 110 and 104 volts respectively, thus showing that each of the two parts was much greater than the whole. On joining a condenser and inductive coil in parallel, an ammeter in the main circuit indicated 5.5 amperes, whilst those in the branches showed 6.4 amperes passing through the condenser, and 10 amperes through the coil. Other experiments of a similar nature were described, and it was pointed out that the ratio of the sum of the two parts to the measured total may be large, being about 8 in the case first mentioned. Theoretically, this ratio might be anything, its maximum value being equal to the ratio of the impedance of the coil to its resistance; practically, however, it is not easy to

get this number more than 8 or 10 for ordinary frequencies.

Alternate currents, arcs, and condensers give results of the same general character as those above described, as also do arcs and inductive coils, such as the regulating coils of lamps; this may cause considerable error in estimating the power supplied to such lamps. The magnitude of the error was found to depend greatly on the quality of the carbons and the character of the arc. With bad carbons and a hissing arc the error was very great, but with good cored carbons, burning steadily, it was not very serious.

Combinations of inductive and non-inductive coils exhibit marked peculiarities, particularly if the inductive one be a transformer coil. This last arrangement gave distinct evidence of interference, or difference of phase when the secondary of the transformer was open, but when closed, and with a moderate load, the difference of phase disappeared, thus showing, under these circumstances, that the primary coil had no appreciable self-induction.

On the subject of alternator characteristics, a graphical method of drawing the E.M.F. curve from the terminal curve was described, and the dependence of the terminal curve on the character of the external circuit pointed out. Keeping the speed, exciting current, and armature current constant, the pressure between the terminals was shown to be dependent on whether the external circuit consists of condensers, resistances, or inductive coils, the pressure being greatest in the former and least in the latter. The true E.M.F. of the dynamo, however, was the same in all the cases, but it became less as the armature current increased. From these results, the authors conclude that the drop in E.M.F. with large currents is due to reaction on the field, but that the change of terminal pressure cannot be all attributed to this cause.

Transformers, it was shown, are powerful controllers of phase, for the primary and secondary currents are nearly always circulating in opposite senses: the phase angle for a 1 to 1 Mordey transformer experimented on, varying from 170° at no load to 180° at full load. The relation between the strengths of the primary and secondary currents, $A_p A_s$, was found to be a linear one, of the form—

$$\frac{P}{S} A_p = \alpha + \beta A_s,$$

where P and S are the number of turns in the primary and secondary respectively, and α and β constants; α representing the exciting current, and β being nearly unity. The phase angle, ϕ , between the currents was given by the equation—

$$-\cos \phi = \frac{1 + \beta^2 A_p + \alpha \beta}{\beta A_s + \alpha}$$

The results of numerous experiments on a transformer of the Mordey type, in which coils having different numbers of turns were put in parallel with each other were given. In some cases resistances were put in circuit with the coils, and in others one or more of these resistances were cut out. Remarkable interference effects were thus produced, for in some combinations the volts or currents were additive, whilst in others they were nearly differential.

In connection with the Ferranti effect, experiments had been made by putting a condenser on the terminals of the secondary of a transformer, and noting the resulting increases in pressure, both in the primary and secondary circuits. The results obtained with a given condenser and approximately constant secondary pressure show:—

1. That whether the transformation be up or down, the percentage rise in the secondary is greater than that in the primary.
2. That these percentage rises diminish as the secondary current increases.
3. That they increase with the ratio of transformation.

4. That the rise in the secondary may be considerable, without that in the primary being appreciable.
5. That the rise in the secondary still persists even when large currents are flowing.

These facts lead the authors to believe that the "Ferranti effect" is due to some kind of interaction between the cable condenser and the self-induction of the transformer, and that is not wholly due to armature reactions in the dynamo.

In the discussion on the paper, Mr. SWINBURNE said the character of the "Ferranti effect" had been wrongly stated, for he understood Prof. Ayrton to say that the pressure between the Ferranti mains was greater at the London end than at Deptford. This, he contended, was impossible. He also said the effects now described, of putting a condenser on the secondary of a transformer and noticing the rise in both primary and secondary volts, were due to the waste field of the transformer. In large transformers, such as those at Deptford, the magnetic leakage was proportionately much less, and no such effects would be noticeable with them. Referring to the relation between the primary and secondary currents in transformers, he said it was convenient to look at the primary from two points of view, and consider one part of it as producing the magnetisation and the other as neutralising the effect of the secondary current.

Mr. MORDEY described an experiment on armature reactions in alternators, in which one of the armature coils of a 50 H.P. machine was isolated from the rest and connected directly to a Cardew voltmeter. On varying the load from 0 to the full output (20 ampères), the voltmeter on the isolated coil was quite stationary, thus showing that no appreciable armature reaction occurred.

Mr. E. W. SMITH remarked that the formula connecting the primary and secondary currents holds true over a very wide range, for he had experimented on a Kapp transformer, which gave (a) constant and (8) = 1 for frequencies varying from 20 to 200.

Mr. BLAKESLEY gave the following formula as applying to transformer currents generally:—

$$\left(\frac{A_p}{A_s}\right)^2 = \frac{n^2}{m^2} \left\{ (1 + k r_s^2) + \frac{q r_s^2}{v} \right\};$$

where r_s = resistance of secondary, v is proportional to the frequency, m and n the primary and secondary turns, and k and q are the constants depending on the disposition of the iron. This formula he found to very nearly represent Ferrari's results, and he hoped others would test its applicability to various types of transformers. He believed himself to be the first who carried out an interference experiment, when he put a condenser in parallel with an inductive coil, six years ago. He mentioned the matter now because that arrangement had been put forward by Mr. Glazebrook in explanation of the "Ferranti effect." Mr. Glazebrook, however, had made an error in stating that under certain conditions one of the currents may become infinite.

Dr. THOMPSON thought the word interference had been used in a somewhat different sense to its ordinary usage in optics, and asked for an authoritative definition of its meaning in the paper under discussion. The experiments on the alternating arc he considered very remarkable, as well as those on the dynamo, which give various terminal pressures when its E.M.F. and current were the same, but the external circuit of different character.

Prof. AYRTON pointed out that the measurements on the rise of volts by putting on condensers, mentioned in the paper were not strictly analogous to those made by Mr. Ferranti, for his were made by pilot transformers, one placed between the primary terminals of the Deptford transformer, and the other on the secondary of the London transformer; whereas in the cases now brought forward the volts measured were those at the primary and secondary of the same transformer. On the subject of arc lamps, he said that Messrs. Kolkhorst, Thornton, and

Weekes, who made the experiments, found that great lag only occurred when the carbons were bad and the arc hissing. If the apparent and the true power spent in such an arc were measured, a great difference existed between them. Dr. Hopkinson, he said, had shown that this might be expected if the arc had a constant back E.M.F. which changed sign with the direction of the current.

A paper on "The Theory of Dissociation into Ions and its Consequences," by Prof. S. U. Pickering, F.R.S., and another on "Some Points on Electrolysis," by Mr. J. Swinburne, were postponed.

Addendum to Report, February 27th, 1891.—The transformer on which the tests described in Prof. Ayrton and Mr. Taylor's paper were made was of the Mordey type, having been kindly lent by the Brush Electrical Engineering Corporation.

CORRESPONDENCE.

DR. CARRINGTON BOLTON'S "CATALOGUE OF SCIENTIFIC AND TECHNICAL PERIODICALS."

To the Editor of the Chemical News.

SIR,—My letter in the CHEMICAL NEWS (vol. lxiii., p. 71), giving some account of my Catalogue of Scientific and Technical Periodicals, 1665—1882, and the chronological tables contained therein, has brought me several communications from both England and America, making inquiries as to the price of the work and the method of securing a copy.

I therefore beg leave to inform such correspondents through your columns that this volume can be had by applying to the secretary of the Smithsonian Institution, Washington, D.C., or for the convenience of residents of Great Britain to the agents of the Smithsonian, Messrs. Wm. Westley and Son, 28, Essex St., Strand, London. The price is 3 dollars or its equivalent. I may be allowed to add that I have no financial interest in the work, and I gave the MS. to the Smithsonian for the convenience of scholars.—I am, &c.,

H. CARRINGTON BOLTON.

University Club, New York, U.S.A.,
March 2, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxii., No. 7, February 16, 1891.

On the Conductivity of the Organic Acids and their Salts.—Prof. Ostwald.

Reply to the Preceding Paper of Prof. Ostwald's.—Daniel Berthelot.—A continuation of the controversy opened in the memoirs on pp. 229 and 230 of the present volume.

On Certain Compounds of Pyridine.—Raoult Varet.—An account of pyridine bromo-cadmiate, of argento-pyridic cyanide, pyridine cyanomercurate, cyanocuprite, and iodocuprite.

On Sodium Amidide and on a Disodammonium Chloride.—M. Joannis.—Sodammonium is decomposed

spontaneously at common temperatures into hydrogen and sodium amide, NH_2Na . This change takes place in the dark as well as in the light, though rather more rapidly in the latter. It appears to tend towards a limit in proportion as the pressure of the hydrogen liberated increases.

Researches on Red Oil (Turkey Red Oil).—M. Scheurer-Kestner.—(See p. 134).

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iv., No. 11.

Action of Isopropyl Iodide upon Aqueous Ammonia in Equimolecular Proportions above 100° . Limit to the Progression of the Isopropylamines.—H. and A. Malbot.—The reaction studied yields chiefly monoisopropylamine hydriodate with a perceptible though smaller proportion of di-isopropylamine hydriodate. The proportion of the latter compound is limited by the work of destruction and reproduction which it undergoes in presence of isopropyl iodide, the consequence of which is the formation of an increasing quantity of propylene.

Transformation of Isobutyl Chloride at 100° in a Closed Vessel in Presence of Aqueous Ammonia. Influence of Time and of an Increasing Proportion of Ammonia.—H. Malbot.—Not adapted for abstraction.

On Alcoholic Fermentation and the Transformation of the Alcohol into Aldehyd occasioned by *Saccharomyces Albicans*.—G. Linossier and Gabriel Roux.—This microphyte causes fermentation in glucose, levulose, and maltose; it is developed at the exposure of saccharose, but without occasioning either inversion or fermentation. Lactose is not affected. Besides the sugars, properly so called, a certain number of substances may serve as a hydrocarbonic nutriment for this *Saccharomyces*, but without undergoing fermentation. Such are dextrine, mannite, alcohol, sodium lactate, lactic acid, gum, and glycerin. Tartaric acid and the tartrates form the outside limit of the substances upon which this microphyte can nourish itself. Starch, erythrite, acetic acid and its salts, oxalic acid and the oxalates, aldehyd, acetone, and the aromatic bodies in general do not nourish the *Saccharomyces albicans*. Besides the secondary products of normal alcoholic fermentations, such as glycerin and succinic acid, we find in liquids which have undergone the action of this ferment a considerable quantity of acetic acid and acetaldehyd.

Can Ozone be Formed on Lowering the Temperature of Flame? Is there Ozone near the Flame?—Prof. Ilosvay de N. Ilosva.—The author criticises the affirmative conclusions of O. Loew and of F. Cundill. All the researches which he has lately made strengthen his conviction that brisk combustion cannot be the source of the ozone supposed to be in the air. Our heating appliances are not fitted up in such a manner that the air mixed with the products of combustion can withdraw from the flame immediately after the reduction of its temperature to that of the decomposition of ozone, and if this could happen the reductive products of the fuel would quickly destroy it. Again, if the combustion were effected in the open air a perfect hurricane would be required to lower the temperature of a flame of a large surface without the condition just mentioned being fulfilled.

Determination of Sulphur not Combined with Hydrogen in Coal-Gas.—Prof. L. Ilosvay de N. Ilosva.—This paper will be inserted in full.

On Certain Combinations of Camphor with the Phenols and their Derivatives.—E. Léger.—The compounds studied are monacamphoric phenol, hemi-camphoric phenol, monacamphoric resorcin, bicamphoric resorcin, the α and β camphoric naphthols, camphoric salicylic acid, and camphoric salol.

On a very Sensitive Reaction of Tartaric Acid.—Ed. Mohler.—If we throw a few crystals of tartaric acid into a sulphuric solution of full strength containing 1 per cent of resorcin, and apply heat, there is produced at about 125° a fine violet-red colouration which may be preserved indefinitely on dilution with acetic acid, but which is at once destroyed on adding water. In order to detect $\frac{1}{100}$ milligramme of tartaric acid, it is needful to evaporate the liquid to dryness in a small porcelain capsule, to moisten the residue with 1 c.c. of the sulpho-resorcin reagent, and to raise the temperature gradually to $125-130^\circ$. Reddish stripes appear first at the bottom of the capsule, and the entire liquid becomes coloured. The reagent has no action upon succinic, malic, citric, and benzoic acids. The mineral acids do not interfere, except the nitric and nitrous acids, which give with resorcin a blue colour so intense as to mask the reaction.

On the Sulpho-Conjugated Phenols or Campho-sulpho-Phenols Derived from Ordinary Camphor.—P. Cazeneuve.—The author gives an account of amethylcamphophenol sulphone, of amethylcamphophenol-sulphonic acid, of camphophenol-trisulphuric acid, of camphophenol sulphuric acid, and of a distinct compound to which he also gives the name last mentioned.—*Bull. de*

Series 3, Vol. iv., No. 12.

Contributions to a Knowledge of the Diphenylic Bases.—E. Noelting and Paul Werner.—The authors have studied di-tolidine (an isomer of ortho-tolidine), bromo- and iodo-diphenylene, the transposition of meta-di-iodazobenzene, and of azobenzene parasulphonic acid, the diphenylic bases obtained by means of oxyazo derivatives, and further a number of derivatives of phenol, of ortho-cresylol, and of para-cresylol.

On the Formation of Diphenylic Derivatives by Means of the Ethers of Hydroquinone.—E. Noelting and Paul Werner.—The substances examined are diethylhydrotoluquinone, diethoxydimethyldiphenylquinone, diethyltetraoxyditolyl, monobromodimethylhydroquinone, dimethylparaxylohydroquinone, diethylparaxylohydroquinone, diethylmetaxylohydroquinone, and diethylorthoxylohydroquinone.

Researches on the Double Rhodium Nitrites.—M. Leidié.—The author describes the double rhodium and potassium nitrite, the corresponding rhodium salt, the rhodium and sodium and rhodium-barium nitrites.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Separation of Iron Sulphide from Calcium Phosphate.—I venture to trespass on your space to enquire what process is recommended for the separation of sulphuret of iron from phosphate of lime? A large deposit of the latter has lately been discovered, but analysis shows that there is enough sulphuret of iron present to destroy its value.—JAS. E. PICKERING.

MEETINGS FOR THE WEEK.

- MONDAY, 22rd.—Medical, 8.30.
Society of Arts, 8. "Photographic Chemistry," by Prof. R. Meldola, F.R.S.
TUESDAY, 24th.—Institute of Civil Engineers, 8.
Royal Medical and Chirurgical, 8.30.
Society of Arts, 8. "Uses of Cloisonné or Decoration in Ancient and Modern Times," by Clement Heaton.
WEDNESDAY, 25th.—Chemical Society, 8. (Anniversary Meeting)
Election of Office Bearers and Council.
Geological, 8.

THE CHEMICAL NEWS.

VOL. LXIII., No. 1635.

THE ISOMERIC FORMS OF THE HYDRAZON OF ORTHONITROPHENYLGLYOXYLIC ACID.

By A. KRAUSS.

SOME time ago H. Fehrlin showed that this body, if treated in the cold with alcoholic potassa, is converted into an isomeric compound, concerning which nothing definite is known.

If hydrazon is dissolved in an aqueous solution of potassa, and immediately precipitated with dilute acids, the hydrazon is recovered unchanged, but if the solution is allowed to stand, the sparingly soluble potassium salt of the isomer is deposited. The complete conversion in the cold requires some hours. On decomposing the salt with dilute hydrochloric acid, the isomer is obtained as a yellow powder, which, after re-crystallisation from alcohol, has the melting-point 188° — 189° . Soda effects no change in hydrazon.

The composition of hydrazon is expressed by the formula $C_{14}H_{17}NO_4$. The isomerism is not physical, but chemical.—*Berichte Deutsch. Chem. Gesellschaft*, xxiii.

HYDRAZOIC ACID.

H.H. CURTIUS and Radenhausen have continued the study of this strange compound, HN_3 , and have communicated their results to the *Journal für Prakt. Chemie*. This acid, when anhydrous, is gaseous at temperatures above 37° , but on cooling it condenses to a very explosive gas. In the Torricellian vacuum it explodes, as also under a variety of conditions not as yet thoroughly determined. This behaviour has already occasioned one very serious accident, Dr. Curtius being the sufferer. Its explosive force is very violent. In one case every article of glass was not merely shattered, but pulverised.

The azoates, e.g., $BaNg$, explode if exposed to a strong green light. The silver salt behaves in a very similar manner.

The acid is found to be stronger than the acetic, and it possesses one property which it is surprising to find in any acid of organic origin, or, indeed, in any single acid. Its aqueous solution dissolves gold, forming a red salt. It seemed not unlikely that the ammonium salt of the new acid might yield an isomeric compound analogous to urea, but this is found not to be the case.

The first method taken for obtaining the free acid was by the action of dilute sulphuric acid upon the sodium salt. An improved process sets out from the hydrazine derivative of hippuric acid, which is converted into a nitroso-derivative by treatment with sodium nitrite and acetic acid at a temperature about 0° . The crystalline compound obtained is dissolved in aqueous caustic soda, and dilute sulphuric acid is then let fall drop by drop into the solution, which is kept at a boil. Weak hydrazoic acid distils over and is allowed to flow into a solution of silver nitrate, forming N_3Ag . This salt is dried at a temperature of 60° — 70° , and is then decomposed by dilute sulphuric acid.

The name adopted for this compound is not very happy, since the "azoates" may easily be confounded with "azotates"—the French name for nitrates. Further discoveries on this acid and its salts may be expected.

AN IMPROVED METHOD FOR THE SAPONIFICATION OF TALLOW TO ASCERTAIN THE SOLIDIFYING POINT OF ITS FATTY ACIDS.

By H. N. WARREN, Research Analyst.

THE action of the fixed alkalies upon the fatty bodies in general, as is well known, results in the formation of a soap corresponding to the alkali employed; and since the production of these compounds are necessary, in order to produce and examine further their allied acids, so as to ascertain the solidifying point of the same, an accurate and expeditious method of saponification should be considered by no means unwelcome.

The simplest method of saponification recorded is that of boiling for a considerable period a sufficiency of the sample under examination in contact with an excess of caustic soda. This reaction, as granted, proceeds tranquilly until the formation of a certain quantity of soap has been reached; the remaining unsaponified fat becomes then in a large manner protected by mixing intimately with the resulting soap, and thus escaping for some time the further action of the alkali. To obviate this an alcoholic solution has been employed; this may have preference over an aqueous solution, but its drawbacks, on the other hand, are twofold. Only quite recently during the examination of a number of samples of tallow, the author accidentally employed for saponifying the same a combined mixture of caustic potash and soda, and being struck with the ease with which they saponified was led to adopt this method in preference to others. The operation is conducted by selecting about 20 grms. of the sample, introducing the same into a copper pan containing in excess a boiling solution of equal parts of potassium and sodium hydrate; a complete saponification of the fat is brought about by exposing the same for about ten minutes at the boiling-point. To the contents are then added a slight excess of dilute sulphuric acid, and the heat maintained until the fatty acids thus separated float uniformly upon the surface of the liquid, the acids being afterwards washed by means of hot water in a separating funnel, until free from impurities. They are then introduced into a flask of convenient dimensions surrounded by salt water and raised to an elevated temperature by boiling the same, during which time a slow current of air is injected through a glass tube into the flask; by this means the whole of the moisture is expelled, and the solidifying point observed in the usual manner. By this means I have worked as many as twenty samples in less than five hours.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

ON THE INFLUENCE OF PRESSURE ON THE SPECTRA OF FLAMES.*

By G. D. LIVEING, M.A., F.R.S., Professor of Chemistry, and J. DEWAR, M.A., F.R.S., Jacksonian Professor, University of Cambridge.

WE have already described (*Phil. Trans.*, A, 1888) the remarkable spectrum of the oxy-hydrogen flame burning at the ordinary atmospheric pressure. Recently we have examined the spectrum of the same flame at various pressures: hydrogen burning in excess of oxygen up to a pressure of 40 atmospheres, and oxygen in excess of hydrogen up to a pressure of 25 atmospheres, also that of the mixed gases burning in carbonic acid gas.

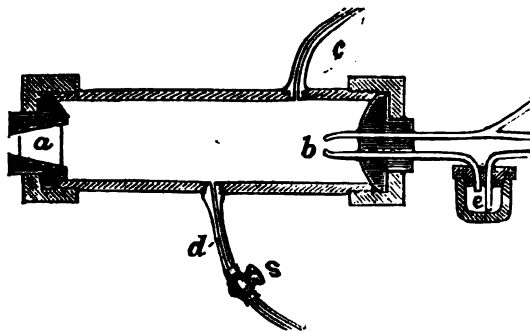
The apparatus employed was an adaptation of one of the tubes used in our experiments on the absorption spectra of compressed gases (*Phil. Mag.*, September, 1888,

* Abstract of a Paper read before the Royal Society, Feb. 19, 1891.

and *Roy. Soc. Proc.*, vol. xlv., p. 222). It consisted of a steel cylinder, about 50 m.m. in internal diameter, and 225 m.m. long, fitted at one end with a quartz stopper, *a*, in the annexed figure, and with a jet, *b*, for burning the gas, adapted by a properly fitting union joint to the opposite end. There were two tubes, *c* and *d*, connected to the cylinder at the sides, of which one, *c*, served for the introduction of gas, while the other, *d*, was fitted with a stopcock and was used to draw off the water formed, or to reduce the pressure of the gas in the cylinder if that was desired. The flame was observed, nearly end on, through the quartz stopper. The whole apparatus was kept cool by a stream of cold water running on to a sponge cloth wrapped round the cylinder. In the course of the tube conveying gas to the jet *b* was interposed a small cylinder, *e*, in which sodium was placed, and by heating this, the gas entering could be charged with sodium vapour.

The gases were supplied from steel cylinders into which they had been compressed, and the pressure was registered by a gauge attached to the tube by which the gas entered the experimental cylinder. Commercial compressed gases were used, containing a sensible percentage of air.

When hydrogen was the gas forming the burning jet, it was lighted at the end of the tube *b* before introducing it into the experimental cylinder. When it was desired to have a jet of oxygen burning in hydrogen, this could be managed by introducing oxygen through the second tube and increasing the supply of hydrogen until the flame



passed over to the oxygen jet. The same result was sometimes attained by first filling the experimental cylinder by a gentle stream of hydrogen through the side tube *c* before the end with the tube *b* was screwed on; the hydrogen as it issued was then lighted, and the jet, with a gentle stream of oxygen issuing, inserted and screwed down. The stopcock, *s*, was kept open until this was done, and then by closing *s*, and admitting more gas from the reservoirs, the pressure in the experimental cylinder could be increased at pleasure.

Hydrogen Burning in Oxygen.

The first observations were made with a jet of hydrogen burning in oxygen. As the pressure rose, the luminosity of the flame increased, as long ago described by Frankland (*"Experimental Researches,"* p. 905). The colour of the flame, viewed end on, was yellow, as if it contained sodium; but on examining it with a spectroscope, it was found to give a continuous spectrum intersected by many shaded bands, and the D lines of sodium were only faintly present. The shaded bands were faint at a pressure of 5 atmospheres, but at pressures of 20 atmospheres and upwards they came out strongly. They were evidently the absorption bands of NO_2 , derived from the residue of atmospheric air mixed with the condensed gases. We took a photograph of them, and on comparing this with a photograph of the NO_2 bands, we found the two to be identical. Except for the bands, and the bright lines of sodium, the spectrum appeared to be continuous, and to extend from about λ 6200 to λ 4150, with the brightest

part about λ 5150. It increased in brilliance as the pressure increased, as well as in extent, being visible at 3 atmospheres pressure from about λ 6720 to λ 4040. The greater distinctness of the NO_2 bands at the higher pressures was due both to the greater brightness of the continuous spectrum and to the greater quantity of NO_2 formed. A large quantity of water accumulated in the experimental tube, and when this was drawn off by the stopcock, *s*, it effervesced with escape of NO , and was found to be strongly acid. A specimen titrated was found to contain very nearly 3 per cent of nitric acid. The observations were continued up to a pressure of 40 atmospheres. There was no indication that the continuous spectrum had any connection with the line spectrum of hydrogen. There was no increase of brilliance in the neighbourhood of the C, F, or G lines of hydrogen. The characters of the spectrum were, however, better seen in the absence of NO_2 , and will be described in the next section.

Oxygen Burning in Hydrogen.

In this case the colour of the flame was very different from that of hydrogen burning in oxygen. Instead of being yellow, it appeared, to the unaided eye, to have a lavender hue. In the spectroscope it showed a perfectly continuous spectrum, brightest in the green, about the region of the Fraunhofer line *b*, and very gradually fading away on either side. On the red side it could be just traced up to about λ 6150, and on the violet side to about λ 4285, at ordinary pressures. The sodium lines were absent. With increase of pressure it increased very much in brightness, and at 8 atmospheres pressure it could be traced as low as λ 6630 and as high as λ 3990.

The dispersion used was that of a direct-vision spectroscope (such as was described by us, *Roy. Soc. Proc.*, vol. xli., p. 449), equivalent to three prisms of white flint glass, but the collimator and telescope very short, so as to obtain plenty of light. With less dispersion, perhaps, the continuous spectrum might have been traced further. Photographs, however, showed that it scarcely extended into the ultra-violet. There was no indication that this spectrum was due to an expansion of the lines of either the first or second spectrum of hydrogen. It is true that the maximum brightness (which could not be determined with any great accuracy) was not very far from F, but no indication of any second maximum in the neighbourhood of either C or G, or anywhere else, could be detected. The pressure was carried up to 12 atmospheres, and at this pressure the visible spectrum was brilliant, but in the ultra-violet, photographs showed that the spectrum consisted only of what we have called the "water-spectrum," very strong and sharp. The lines of this spectrum showed no signs of expansion even at a pressure of 12 atmospheres, and, though much more intense than at ordinary pressures, remained clearly defined.

Observations were continued with the eye up to 35 atmospheres pressure, but no trace of emission, or absorption, corresponding to either spectrum of hydrogen, could be detected, and it is doubtful if either spectrum can be produced in such a flame. Since the formation of steam from its component gases is attended with a diminution of volume, increased pressure will increase the stability of the compound, and the flame will contain a larger proportion of steam, as well as have a higher temperature, than at ordinary pressures.

The water formed when the flame was a jet of oxygen burning in hydrogen was found to be alkaline, and to contain ammonia. But the proportion of ammonia was much less than the proportion of nitric acid formed when the jet was hydrogen burning in oxygen; a specimen titrated contained 0.0004 per cent of ammonia.

Effects of Pressure on the Sodium Spectrum.

In order to see what effect would be produced by increased pressure on the spectrum of other substances in the flame, we charged the hydrogen with sodium vapour by making it pass, before entering the experimental

cylinder, through a small iron cylinder, *e*, in the figure, containing metallic sodium, heated by a lamp. As the D lines of sodium are very easily expanded and self-reversed in a flame at ordinary pressure, some care was needed to discriminate the effects which were really to be ascribed to pressure. The gas was easily charged with sodium vapour, and when burning in oxygen, not only the D lines, but the citron and green pairs, and sometimes the blue pair (λ 467), and the orange pair (λ 616), were well seen; but we could not find that they were expanded by increase of pressure. A sudden change of pressure generally produced an expansion, but it did not last; the lines fined down again when the pressure was steady, whether that pressure was high or low. These experiments were continued up to a pressure of 40 atmospheres without any definite effect on the width of the lines which could be ascribed to the pressure.

It may be said that at the higher pressure the evaporation of the sodium would be slower, and so the proportion of sodium vapour to hydrogen be diminished; also, when the lines are diffuse at the edges to begin with, it is extremely difficult to judge whether there is any expansion. At all events, we may say that there is no expansion produced by pressure at all comparable with that produced in a flame at ordinary pressure by increasing the quantity of sodium in the flame. We noticed, however, that the presence of sodium, which produces a feeble continuous spectrum in a flame at an ordinary pressure, seemed to increase the continuous spectrum of the flame under pressure, especially in the orange and green.

(To be continued).

ON THE POTASSIUM CYANIDE ASSAY OF LEAD ORES.

By ARTHUR W. WARWICK,
Assayer at the Phoenix Test Works, Battersea.

(Concluded from p. 30).

OWING to press of other work, I have been unable to finish the experiments upon the cyanide assay of lead quite as soon as I expected. The experiments have been continued upon the remaining ores of commercial value, viz., anglesite, pyromorphite, and mimetisite, and with the two former minerals results have been obtained exceeding all expectations. As was to be expected, with the last named mineral, the result was vitiated owing to the reduction of arsenic, giving too high a result. The lead-antimony minerals such as jamesonite, &c., were not treated, since the lead and antimony would be reduced together. Of course, the lead and antimony might be estimated in the button by the usual wet process, but such a mode of procedure offers no advantage over the usual chemical analysis.

Anglesite.—The anglesite employed for the following experiments contained a small quantity of cerussite, and here and there a minute crystal of galena was seen glistening. It contained 59.62 per cent of lead as shown by chemical analysis. The mineral was crushed and passed through a 60 sieve, samples being taken when required by the method detailed in my first paper (CHEM. NEWS, vol. lxiii., p. 30). 100 grains of the ore were mixed with 600 grains of "stick" KCy, and placed in a small Battersea crucible with the precautions observed in the galena assay. This mixture was heated for twenty minutes, using a low red heat rising gradually to a bright red. A good finishing temperature was required, otherwise the slag would have been too viscid. The button of lead was obtained in the usual way by breaking the crucible.

Exp. No.	Grains.
21. Button of lead obtained	59.3
22. " " "	59.4
Mean 59.35 p.c.	

The slag was of a light pink with a white crystalline core. This result is as good as it is possible to get with any furnace assay, since it is only 0.27 per cent below that given by chemical analysis.

Pyromorphite containing 74.01 per cent of lead was the mineral next worked upon. A sample was made as above, and 100 grains of the ore treated, in duplicate, as in experiments 21 and 22, finishing, however, with a moderate red heat. The crucible showed only a spongy mass at the bottom instead of the expected button. Further experiments were made using a higher finishing temperature as well as modifying the starting temperature. In experiments 23 and 24 the temperature at the commencement was a low red.

Exp. No.	Grains.
23. Button of lead obtained	72.85
24. " " "	72.70
Mean 72.77 p.c.	

In experiments 25 and 26 a moderate red heat was used at the start, and finishing at a bright red as in experiments 23 and 24.

Exp. No.	Grains.
25. Button of lead obtained	73.0
26. " " "	73.1
Mean 73.05 p.c.	

The mean of five experiments gave a result of 73.1 per cent. From these experiments it is obvious that a higher temperature is required to complete the reaction with pyromorphite than with any of the preceding minerals. The result is rather astonishing considering the high temperature used, and certainly points to the loss in the galena assay being a chemical one, and not so much to loss by volatilisation. This assay yields 0.91 per cent lower than the chemical process. For comparison, two assays were made, using the mixture of

Ore 200 grs.
Carbonate of soda .. 250 "
Argol 60 "

Covered with 100 grs. borax.

This mixture was fused for twenty-five minutes, using a bright red heat, and the fused charge poured into a warm mould. The following results were obtained:—

Exp. No.	Grains.
27. Button of lead obtained	142.2
28. " " "	141.9
Mean 71.05 p.c.	

The slag thus obtained is viscid, and there is great danger of it enclosing small globules of metal unless the crucible is handled rapidly. This result is 2.06 per cent below the cyanide method.

A sample of impure mimetisite was next experimented upon, with, however, very varying results. The button of lead obtained was brittle and of a very dark colour, due to the presence of arsenic. Under these circumstances, after making four experiments with similar results, no more work was done upon this mineral.

The fact that one flux gives good results with all the commercial ores of lead is of great value. As galena, cerussite, and anglesite frequently occur together, it is of great advantage to be able to assay all these minerals with the same flux. Of course this method does not give such accurate results as the sulphate chemical method, but as the furnace method is still largely used (and in all probability will continue to be used) in most lead mines, any method which will give higher results than those now in use is well worth considering.

It is true, as Mr. Cooper states (CHEM. NEWS, vol. lxiii., p. 73), that with lead ores containing other reducible metals the lead button obtained contains a notable quantity of those metals. In those cases where the impurity is large, the furnace method is inapplicable, and the chemical method must perforce be employed. The galena

used in experiments 15 and 16* contained nearly 2 per cent of copper pyrites, and most of the copper was in all probability carried off in the slag, as the lead button obtained was quite clean and soft. Percy made a number of experiments some years ago in the Metallurgical Laboratory of the School of Mines upon cupriferous galena. A galena containing 10 per cent of copper pyrites was reduced, using a carbonate of soda and argol flux, and the amount of copper determined in the button of metal obtained. It was found that the button of lead contained 98.9 per cent of lead and 1.1 per cent of copper; with a galena containing 25 per cent of pyrites; the button of metal contained 96.5 per cent of lead and 3.5 per cent of copper, the rest of the copper being contained in the slag. From these figures it is evident that with a galena having less than 5 per cent of copper pyrites the error introduced is negligible, since the button would contain less than 0.4 per cent of copper. I may point out, however, that the quartz worked on by Mr. Cooper could hardly be called a lead ore, inasmuch as it only contained 3 per cent of galena and about 10.5 per cent of copper pyrites; surely this is more like a copper ore. The results obtained from a mineral of this character do not warrant the condemnation of the cyanide assay of lead ores.

DETERMINATION OF FERRIC OXIDE AND ALUMINA IN PRESENCE OF PHOSPHORIC ACID, ACCORDING TO THE MOST RECENT RESULTS.

By Dr. von GRUBER.

THE determination of ferric oxide and alumina in phosphates is of the greatest importance for the manufacture of superphosphates, as it is the only method of foreseeing the results of the process and the value of the finished article. Even the phosphoric acid which has been rendered soluble goes back and becomes insoluble in proportion to the proportion of ferric oxide and alumina in the manure.

This fact is admitted, although the process of reversion is still unexplained. The author suggests that the strong attraction of water by the gypsum as it passes from the precipitated to the crystalline state deprives the existing phosphates of sesquioxides of their constitutional water, and thus converts them into an insoluble modification; at least certain experiments made point in this direction. The object of the present communication is to discuss the methods of determining the sesquioxides which have only just been perfected, which, considering the practical importance of the question, is truly surprising.

There has been hitherto employed a so-called "conventional method," the result of which showed the most striking discrepancies. It was customary to dissolve in acetic acid the precipitate obtained by adding ammonia to the hydrochloric (or nitro-hydrochloric) solution of the phosphate, containing the phosphates of the alkaline earths, of ferric oxide, and alumina. Calcium and magnesium phosphates were supposed to be completely dissolved, whilst ferric and aluminium phosphate remained undissolved. But as a considerable quantity of calcium phosphate always remained in the precipitate the precipitate was re-dissolved in hydrochloric acid, re-precipitated with ammonia, and the precipitate dissolved a second time with acetic acid. The precipitate was thus rendered purer, and was, indeed, generally free from lime; but whilst the first result was too high in consequence of the presence of calcium phosphate, the second precipitate gave too low a result, as the cold acetic acid has a solvent action, especially on the aluminium phosphate.

Still this conventional method was retained, though it could not claim the rank of a scientific process, and must

even be regarded as insufficient for the demands of practice. There was no other method of determination.

From this point of view we can understand the discrepancies announced from the laboratories of leading analysts:—

	A.	B.	C.	D.	E.
	Per cent.				
I.	0.60	0.56	0.23	0.39	2.67
II.	0.85	—	0.26	—	—
III.	1.38	2.93	0.93	0.99	3.40
IV.	—	—	—	—	0.60

The letters A—E stand for the various materials examined, and the numbers I.—IV. stand in place of the names of the analysts. It is seen that there can scarcely be any idea of an agreement. It seems as if one analyst had precipitated only once and others twice.

Whilst making known these conflicting results the author endeavoured about six years ago to draw attention to the unsatisfactory nature of this method of determination, and expressed the wish that as long as no better process was known this "conventional method" might be developed by fixing exactly the quantity of acid to be used for the crude phosphate, the quantity of ammonia to be used for neutralising, and the quantity of acetic acid, so that the results obtained might at least be concordant if not strictly correct. He also made the request that the experience gained in seeking for a better method might be mutually communicated.

Not one reply was obtained to this circular letter sent out by the author and his collaborator, Herr Otto Schönherr, though he does not venture to infer that the subject was ignored. There was never found an absolutely correct result even when working with pure materials. Among other expedients he tried the precipitation of the phosphoric acid of the precipitate with molybdenum as proposed by Stutzer. The worst point was that no explanations for the deviations—often considerable—could be given.

The method of Eugen Glaser (published in November, 1889) solved the question in a manner sufficiently accurate for technical purposes, and avoided the errors of the conventional method. This so called "alcohol method" is very simple:—

5 grms. phosphate are dissolved in the usual manner in 25 c.c. nitric acid of sp. gr. 1.2, and about 12.5 c.c. hydrochloric acid of the same sp. gr., and made up to 500 c.c.; 100 c.c. of the filtrate (= one-fifth of the sample) are placed in a $\frac{1}{2}$ -litre flask, with the addition of 25 c.c. sulphuric acid of 1.84 sp. gr. The flask is let stand for five minutes, shaking occasionally; about 100 c.c. alcohol (95 per cent) are added; the flask is cooled, filled up to the mark with alcohol, and well shaken up. After standing for half an hour the liquid is filtered. 100 c.c. of the filtrate (= 0.4 gm. of the sample) are evaporated down in a platinum capsule until the alcohol is expelled. The solution is then mixed with 50 c.c. water in a beaker and heated to a boil. Ammonia is added to the solution until the reaction is alkaline, but not whilst boiling, to avoid a violent effervescence.

The excess of ammonia is boiled away; it is let cool, filtered, the precipitate washed with hot water, ignited, and weighed as ferric and aluminium phosphate. On trying this method the author obtained results which agree with those of calculation. The precipitate obtained was pure, consisting entirely of ferric and aluminium phosphates.

In January, 1890, Stutzer published another method for the determination of ferric oxide and alumina in phosphates. The first (calciferous) precipitate which remained on precipitation with ammonia and treatment with acetic acid, is collected and treated with molybdic solution in the usual manner to remove the phosphoric acid. In the filtrate the ferric oxide and alumina are precipitated with ammonia in the usual manner.

This method seems, theoretically speaking, to ensure

absolutely correct results. In the meantime the author has tried it years ago, and not obtained satisfactory results. On repeated trial it was the same. Sometimes he obtained several satisfactory analyses in succession, but then all at once the method failed without any perceptible reason. Dr. Stutzer himself has had similar experiences; whence the method cannot be pronounced satisfactory until the necessary precautions have been discovered. However, a combination of Glaser's method with that of Stutzer meets the objection that half the quantity of ferric and aluminium phosphate found is calculated as sesquioxides. This objection is justified in view of the different molecular weights of ferric oxide and alumina if scientific accuracy is required, but for technical purposes no scruples need be entertained. If it is necessary to remove the error the precipitate obtained, according to Glaser's method, which is free from lime and magnesia, is re-dissolved and treated with molybdic solution, so that the pure sesquioxides can be precipitated from the filtrate with ammonia and separated in the usual manner.

The "alcohol method" was formally accepted at the Congress of German Experimental Stations held on September 18th.—*Zeitschrift Anal. Chemie.*, xxx., p. 9.

DISCUSSION ON THE THEORY OF SOLUTION.*

The following discussion ensued on the reading of the paper on "The Present Position of the Hydrate Theory of Solution," by Mr. S. U. Pickering, F.R.S., which appeared in the *CHEMICAL NEWS*, vol. lxii., pp. 185 and 194:—

Dr. GLADSTONE made a communication on "The Molecular Refraction of Substances in Solution," in which he reconsidered the five reasons given in 1865 and 1869 for believing that "the specific refractive energy of a solution is the mean of the specific refractive energies of the solvent and the substance dissolved." In describing the present state of our knowledge, he brought forward some facts which have a bearing on the views under discussion.

In the first place, although it may be accepted as a rule that a solid when dissolved retains its former refractive power, it is a rule not without exceptions. Thus the experiments, both of the speaker and of Dr. Bedson, on rock salt agree in giving 14.6 as the molecular refraction of chloride of sodium for the solar line A or R; in which R

represents the value $\frac{\mu-1}{d}$ multiplied by the molecular weight. But the molecular refraction for the same ray as calculated from aqueous solution is 15.3, showing that the water has perceptibly increased the refractive power. And this is not an isolated instance, for the observations of Topsøe and Christiansen on crystals of potassic bromide and iodide show a molecular refraction for the line D, or λ_D , of 24.85 and 36.29 respectively, while the solutions indicate 25.7 and 36.9 respectively. In fact, the chlorides, bromides, and iodides, in general, when dissolved in water, are known to exhibit a higher refraction and dispersion than would be calculated by adding together the generally received values for the metal and the halogen, and this increase is uniform for each series of salts.

It is also known that there is a slight change in the molecular refraction of certain liquid substances, such as acetic acid, when they are mixed with water.

In the second place the molecular refraction of a substance in solution is not varied by varying the amount of the solvent. In the case of water, however, there are some marked exceptions. With the hydracids the values increase with the dilution up to a certain extent, when they become stationary. Nitric and sulphuric acids are

also exceptional. It is evident that the difference here noted does not depend upon whether these binary compounds are electrolytes or not.

In the third place there is a great deal of evidence that the molecular refraction of a substance is the same whether it be deduced from its solution in alcohol, ether, benzene, bisulphide of carbon, or any other solvent that does not act chemically upon it. The same rule applies in some instances to solution in water; thus the molecular refraction of ammonia in alcohol, or in different quantities of water, was found to be about 8.96. The value for gaseous ammonia, as deduced from Dulong's observations, is 8.60.

A notable exception is hydrochloric acid. Very early in the history of refraction equivalents it was recognised that this acid in aqueous solution gave a value much larger than the gas itself, or than what would be obtained by adding together the values for chlorine and hydrogen in combination, as deduced from other sources. Dr. Perkin found a similar great increase of magnetic rotation in an aqueous solution of hydrochloric acid, but on dissolving the gas in isoamyloxide and examining the solution he found it rotated the plane of polarisation to very little more than the theoretical amount. The speaker therefore determined the refraction of this solution, and found the hydrochloric acid in it to have practically the theoretical value.

HCl, theoretical value	11.2 or 11.3
HCl, in water	about 14.4
HCl, in isoamyloxide	11.36

It would not be safe to use this increase of refraction of hydrochloric acid in aqueous solution as an evidence either of dissociation or of the formation of a hydrate. For the sum of the molecular refractions of free hydrogen and free chlorine, as determined by Dulong or Mascart, would be only 10.3, rather less than the theoretical, instead of more, as might be expected on the dissociation hypothesis,* while, on the other hand, the addition value of H₂O in recognised hydrates (such as crystallised alums) seems to be the same as that of pure water, namely, 5.93.

The general inference drawn by the speaker from the accumulated evidence was that the old conclusion is substantially correct; that molecular refraction and dispersion may be safely deduced from substances in solution where the solvent is chemically inactive, but that in the case of water there is some profound change effected upon the constitution of hydracids, haloid salts, and probably some other compounds by the act of solution. What this change may be cannot at present be inferred from optical analysis.

Dr. JAMES WALKER read the following translation of a communication from Dr. ARRHENIUS:—

"In the *Journ. Chem. Soc.* for 1890, p. 355, Mr. Pickering writes:—'It is indeed surprising that van't Hoff, Arrhenius, and others should not have recognised that every known deviation from the so-called normal depression, when induced by increase of strength of the solution, is in exactly the opposite direction to that which it should be if the law of osmotic pressure were really correct.' That the depression of the freezing-point per grm. molecule should decrease with increasing concentration is no deduction (as Mr. Pickering seems to imagine) from the law of osmotic pressure; and the corresponding statement for the analogous case of highly compressed gases has been proved to be false by the researches of Regnault, Netterer, and others. . . . Besides, it is not correct that 'every known deviation' is in the opposite direction to that expected by Mr. Pickering.

* These numbers would have been brought more closely together if the calculation had been made by means of Lorenz's formula, $\frac{\mu^2-1}{\mu^2+2} \times \frac{1}{d}$ instead of the simpler $\frac{\mu-1}{d}$. With liquids and solids it is practically unimportant which formula is employed.

H ₂ SO ₄ per cent.	Sp. gr.	Gr.-equiv.	i, = 1 + 2a	Freezing-point.			Differences in 1-1000 deg. Cent.	
				Obs. ₁	Obs. ₂	Calc.	Obs. ₁ -calc.	Obs. ₂ -calc.
3'993	1'0278	0'8376	2'036	-1'61°	—	-1'62	-10	—
3'967	1'0274	0'8324	2'036	1'58	—	1'61	-30	—
3'492	1'0243	0'7300	2'042	1'37	—	1'42	-50	—
3'008	1'0210	0'6267	2'051	1'19	—	1'22	-30	—
2'806	1'0193	0'5835	2'058	1'10	—	1'14	-40	—
2'496	1'0174	0'5182	2'064	0'981	—	1'016	-35	—
1'996	1'0140	0'4130	2'082	0'788	—	0'817	-29	—
1'785	1'0126	0'3688	2'088	0'705	0'699	0'731	-26	-32
1'596	1'0112	0'3293	2'094	0'633	0'627	0'655	-22	-28
1'398	1'0100	0'2882	2'102	0'558	0'550	0'575	-17	-25
1'212	1'0087	0'2496	2'112	0'484	0'480	0'501	-17	-21
1'024	1'0073	0'2058	2'126	0'417	0'412	0'416	+1	-4
0'8188	1'0059	0'1681	2'136	0'334	0'332	0'333	+1	-1
0'7138	1'0051	0'1464	2'146	0'297	0'294	0'298	-1	-4
0'6145	1'0044	0'1260	2'156	0'255	0'254	0'258	-3	-4
0'5146	1'0037	0'1054	2'168	0'219	0'217	0'217	+2	0
0'4061	1'0029	0'08312	2'210	0'178	0'177	0'175	+3	+2
0'3562	1'0025	0'07288	2'236	0'160	0'155	0'155	+5	0
0'3063	1'0022	0'06264	2'272	0'138	0'137	0'135	+3	+2
0'2594	1'0019	0'05281	2'304	0'115	0'116	0'116	-1	0
0'2056	1'0015	0'04203	2'352	0'095	0'093	0'094	+1	-1
0'1539	1'0011	0'03144	2'406	0'067	0'072	0'072	-5	0
0'1401	1'0010	0'02861	2'422	0'062	0'067	0'066	-4	+1
0'1012	1'0007	0'02067	2'476	0'052	0'049	0'049	+3	0
0'0771	1'0005	0'01574	2'544	0'038	0'035	0'038	0	-3
0'0519	1'0003	0'01060	2'594	0'026	0'028	0'026	0	+2
0'0264	1'0001	0'00539	2'702	0'016	0'014	0'014	+2	0
				Sum	..	+7	-10	

From Beckmann's excellent determinations (*Zeitsch. fur Physik. Chem.*, ii., 715) it appears that in the great majority of cases the molecular depression does diminish with increasing concentration when benzene and acetic acid are the solvents. Mr. Pickering can find numerous other examples in Eykman's observations, and I shall show below that it is even the case with the sulphuric acid solutions which were the subject of his own investigation.

"Mr. Pickering, in comparing his 'theoretical' with the observed values for the depression of the freezing-point in dilute solution of sulphuric acid, remarks that 'the molecular depression, even in this extreme region,' instead of being constant, as it should be according to the theory of osmotic pressure, varies between 2'95° and 2'1°." Mr. Pickering has overlooked the fact that sulphuric acid is an electrolyte, and that the deviations may be accounted for by the theory of electrolytic dissociation. For the purpose of comparison with the experimental results, I have calculated the values of the depression for dilute solutions, such as Mr. Pickering investigated. In the calculation I have taken the freezing-point of an aqueous solution of a non-electrolyte containing 1 grm. molecule per litre to be -1'90° C., in accordance with van 't Hoff's theory. I have further made the molecular conductivity of $\frac{1}{2}$ H₂SO₄ at infinity dilute (μ_{∞}) equal to 356/10⁷ Siemens's units (Kohlrausch, *Wied. Ann.*, xxvi., 196). From Kohlrausch's numbers we then find the degree of dissociation—

a for 1 0'5 0'1 0'05 0'03 0'01 0'006 0'002*
to be 0'511 0'533 0'585 0'658 0'707 0'802 0'844 0'910

* Normal solutions.

By interpolation we get a for other concentrations (*Zeitsch. f. physik. Chem.*, v., 5). From the percentage composition and the specific gravity (Pickering) I have calculated the number of grm.-equivalents per litre solution. The subjoined table corresponds to that on p. 363 of the *Four. Chem. Soc.*

Mr. P.'s italics.

"Under obs.₁ are the (corrected) observed numbers obtained with thermometer 65108; under obs.₂ are the numbers for the same concentrations interpolated from the series made with thermometer 65561. This comparison affords an indication of the experimental accuracy.

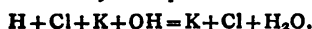
"It is at once evident from the table that the observed numbers agree within the limits of experimental error (obs.₁—obs.₂) with the theoretical values so long as the concentration is less than 1 per cent. The agreement, in fact, is so extremely good as to lead one to put more faith in the calculated than in the observed values. In stronger solutions (1 to 4 per cent) the depressions found are less than the theoretical depressions, in direct contradiction to Mr. Pickering's statement that the opposite is always the case. On this last circumstance, however, we need not lay too much weight, for the theory has not yet been sufficiently advanced in this direction, and the deviations besides only amount here to 3'6 per cent at most. Instead, then, of these experiments of Mr. Pickering finally disproving 'all existing physical (*sic*) theories of solution,' and in especial 'the theory of osmotic pressure,' they afford the most striking proof of the applicability of van 't Hoff's theory and the hypothesis of electrolytic dissociation of dilute solutions, with which alone these theories have hitherto been concerned."

Dr. WALKER drew attention to the fact that in almost all the combinations of solvent and dissolved substance tabulated electrolytic dissociation played a great part, entirely neglected by Mr. Pickering. The comparison of observed with "theoretical" values was thus open to the same objection as Dr. Arrhenius urged in the case of dilute solutions of sulphuric acid, and so the great discrepancies found in the tables were from this cause alone rendered illusory.

Professor RAMSAY suggested that it might well be the case that complex molecular aggregates were capable of existence alongside of dissociated molecules where ions are present. In the case of solutions of sulphuric acid, for example, it is by no means unconceivable that aggregates of several molecules of sulphuric acid (H₂SO₄)_n, or of compounds of acid and water, such as H₂SO₄.2H₂O,

&c., might exist along with the ions of dissociated sulphuric acid $2H$ and SO_4 , or more probably H and HSO_4 . The abnormal results in the freezing-points of solutions of sulphuric acid observed by Mr. Pickering might well be due to some such cause.

Dr. ARMSTRONG, after remarking that thus far the physical aspects of the main problem under discussion—the constitution of solutions which conducted electrolytically—had alone been dwelt on, said that it would be impossible, in the time at disposal, to consider more than one of the conclusions arrived at by the advocates of the dissociation hypothesis, which did not appear to be in accordance with the chemist's experience. It had hitherto been customary to regard the neutralisation of an acid by an alkali as a case of interchange or double decomposition, as represented, for example, by an equation such as $KOH + HCl = KCl + HOH$. But now that it was argued that hydrogen chloride, potassium hydroxide, and potassium chloride underwent almost complete dissociation when dissolved in water to form a dilute solution, it became necessary to suppose that in such cases the only new compound formed in solution was water, and the main action which occurred on mixing solutions of potassium hydroxide and hydrogen chloride was consequently represented by the equation



Such a conclusion, although undoubtedly a necessary and logical one from the dissociationist's point of view, involved the admission that hydrogen chloride and water were compounds of a totally different order; that these two hydrides were so different that while that of chlorine underwent practically complete dissociation that of oxygen remained practically unchanged. Chemists, however, were in the habit of teaching that chlorine and oxygen were comparable elements, and the facts of chemistry appeared to afford the strongest evidence that hydrogen chloride and oxide were in all ways comparable compounds. Moreover the behaviour of the two compounds at high temperatures afforded no grounds for any such belief in the instability of the one and the stability of the other.

Referring to the series of numerical agreements between theory and practice relied on by the dissociationists, the speaker said that in his opinion these afforded no necessary proof of the correctness of the theory. The correlation of chemical activity and electrical resistance which had been established by Arrhenius, Ostwald, and others was undoubtedly of the highest importance, but the successful use which they had made of the data at their disposal appeared to him to depend on the fact that by observations of electrical resistance they were enabled to classify electrolytes in the order of their activity, whether physical or chemical; and that, having done this, they were in a position to apply the correction required to discount the superior activity of such compounds in comparison with dielectrics, *i.e.*, compounds producing the so-called normal effect in depressing the freezing-point, for example.

Professor FITZGERALD said—It is important to distinguish between what is implied and what not by experiments: *e.g.*, osmotic pressure, change of freezing and boiling points are in no way independent; we can deduce one from the other by applying known principles. There seems to be a very important connection, which cannot be deduced from known principles, between conductivity, the variation of osmotic pressure from its value calculated from molecular weights, and the chemical activity of a substance in certain relations. The quality upon which these properties depend is, I think, certainly the same quality in each case, and its existence and importance have been brought to light by the labours of our renowned visitors and their collaborateurs, and the discovery is one of the most valuable contributions to chemical physics that has been made of recent years. The visitors call this quality the "ratio of dissociation." Professor Arm-

strong would rather call it "measure of affinity." I would be inclined to point out that the term "dissociation" is not happily chosen, and that "affinity" really explains very little, and that it would be better to call it by a new name whose full meaning will require further investigation, and would call it "measure of ionisation."

In the first place as to the term "dissociation." In all other cases of dissociation, *e.g.* in an electric arc, the elements are so far free from one another that they diffuse independently of one another. The term "dissociation" is no doubt vague, but it is time we had a more definite notion of it. I would certainly confine the use of the term to such cases that there was no link connecting the elements that would prevent their diffusing independently of one another. As long as there is any link connecting the elements of molecules together which essentially prevented one of them getting away without the others following, I would not agree to say that the elements were dissociated. Hence I object to the term dissociation as applied to the ions in an electrolyte. All agree that one cannot escape or diffuse without the other following; it may be due to electrical forces between them, it may be for other causes; but in either case I would refuse to call them dissociated. The possibility of independent diffusion I look upon as a test of dissociation. I would therefore appeal to both sides to adopt some neutral term such as "ionisation" to express the state of ions in electrolytes. Now as to the proofs that the ions are absolutely independently mobile in the liquid, and the assumption from this that they are free like the molecules of a gas being kept apart by the molecules of the solvent. This seems a very misleading way to speak of the condition. In the first place it is acknowledged that different solvents have different powers of ionising a given substance, thereby conclusively proving that the function of the solvent cannot be properly described as merely giving the ions space to resolve themselves. And those who speak so acknowledge that it is only an analogy, or a *façon de parler*. But it seems a very misleading analogy, which leaves out the really active part that the solvent plays, and attributes to it a purely passive part. The argument of van 't Hoff that the osmotic pressure in very dilute solutions depends only on the kinetic pressure, and not on the forces between the molecules, seems to cut against the conclusion that these forces must necessarily be small; it seems to show that, *whatever* forces there are between the ions, they will produce the right amount of osmotic pressure if only they are so far independent that each ion can carry on its bombardment independently of the other. As this only requires the space within which they are bombarding about to be small compared with the space rate of variation of the force between the elements, and as this is quite consistent with there being plenty of connection between the elements, it follows that the laws of osmotic pressure so explained do not in the least militate against there being bonds between the elements. The whole argument is, however, I think, fallacious, in that it assumes a particular theory as to the action between the semi-permeable membrane and the liquid. It would follow from this theory that one molecule of a salt could never produce osmotic pressure in its own neighbourhood by any forces of attraction between it and the solvent. Now if we apply this on a large scale to the case of an ocean 1000 miles deep surrounding the world with a membrane in it, say, 100 miles deep, through which the water could go, but the world could not because the holes were only, say, about a square mile in area, we see at once that, if this membrane were made of a material lighter than water, *i.e.*, less attracted by the world than water, it would tend to burst out with a great force, *i.e.*, it would float out from the world because the pressure in the water near the earth was much greater than at a distance from it. This shows where van 't Hoff's argument fails. He has neglected the difference of pressure in the solvent near and far from the salt, or at least

has assumed that this difference of pressure could not act upon his semi-permeable membrane because the membrane is permeable to the solvent. It is, however, quite evident that the water can press very hard even on a membrane permeable to it, as is explained by the example I have just mentioned. Considering the complex nature of the problem, I think it is quite too soon to assume that the state of affairs assumed by van 't Hoff is at all like reality. I would much rather look for an explanation in the direction I have pointed out in this year's report of the Committee on Electrolysis. The argument there tends to show that the distances between molecules would arrange themselves so that the forces due to different kinds of molecules would be independent of their kind and depend on their numbers, and this would lead to the laws of osmotic pressure. It seems to me much more likely that a state of affairs such as I have supposed existing near the earth is the one existing in a liquid.

As regards the argument for the independent mobility of the ions founded on the laws of electrolysis, I think that just as in the case of osmotic pressure this does require a certain kind of independent mobility, but just as in that case I do not see that the required amount of independence cannot be attained without supposing a complete independence. There seems no doubt that conductivity and double composition are essentially connected with the same quality in the solution, and this property I have proposed to call "ionisation." Now, Williamson's hypothesis as to the nature of double decomposition and Clausius's as to the nature of electrolytic conduction only require that the ions shall be so far free as that they shall be frequently exchanging partners; neither hypothesis requires that they shall be during a finite time without partners, which I consider to be an essential condition of any right use of the term dissociated ions. If during the time the ions are paired they can move independently within the little chinks they have to move in between the molecules of the solvent—and be it observed that this is the same condition as for the extra osmotic pressure, i.e., if their chinks are small compared with the variation of force between the ions—then there seems quite sufficient independence for any theory of electrolysis, if, whenever two molecules were within the same chink, there were, as there would be, sufficient independence for an exchange of partners. Thus these two phenomena would be explicable upon the same hypothesis, and that without assuming that ionisation was a true dissociation. I have already explained that even those who insist most strongly upon the dissociation hypothesis yet guard themselves from its being supposed that this dissociation is an actually complete independence of the ions from one another. On all these grounds then I would appeal against the use of the word dissociation in this connection. Professor Ostwald says that there will result two theories leading to the same result. I dissent from this. The two theories are essentially the same. There have been unnecessary assumptions no doubt made as to how far an absolute independence of motion of the ions is required by the experiments, and I combat this unnecessarily absolute independence, but in all essential respects my theory is the same as the other. This unnecessarily absolute independence has been introduced in order to make what is acknowledged to be an "analogy" appear as if it were more than an analogy, to give verisimilitude to what is at the same time said to be merely a *façon de parler*, to make what is known to be complicated appear unreal simple.

It may be worth while following Professor Armstrong's suggestions that the way in which the double decomposition is facilitated by a solvent is by the two salts entering into combination with the solvent and forming a large molecule. Then by a process of tautomerism* by which the elements within a molecule exchange places, the double decomposition is effected. A similar but regu-

lated rearrangement under electric forces would account for electrolysis. That solution is a true chemical combination seems undoubted. There is change of nature, e.g., solid salt and ice change into liquid, re-distribution of energy, change of volume, every change significant of chemical action, and that solution can be saturated shows that there is combination in definite proportions, even though some doubt may exist as to the existence of cryohydrates. In speaking of solvents as merely giving molecules space wherein to resolve themselves into ions, it seems as if the part of Hamlet were left out. The action of the solvent is to cause ionisation, some solvents do it and some do not, and it is rather hard on these strangely active solvents not to recognise this activity, one of the most wonderful and effective of all chemical actions known to us.

As regards the energy required for dissociation, or, as I would prefer to call it, ionisation, I agree with Professor Ostwald that any required supply can be obtained by assuming either an affinity of the element for electricity (a form of words I object to for reasons to be presently stated) or by supposing the ionic state to be an allotropic form of the atom with a different internal energy in it from that in the atom when in combination. The reason I object to the term affinity of the atom for electricity is that all we know of electricity seems to show that if any body attracts positive electricity it repels negative, and in that case the atom and its electrical charge combined would not be acted on by electrical forces as is required in order to explain electrolysis. I do not like the idea of an allotropic form of the atom, and think the facts of solution, &c., can all be explained by chemical combination between the salt and its solvent, as I have described, without this assumption. A good deal of weight has been laid on the explanation of the equality of heats of neutralisation of ionised bodies by supposing them to be dissociated. The explanation only pushes the difficulty one step further back. How does it happen that the heats of ionisation or dissociation during solution are many of them so nearly balanced by the allotropic form of the ionic state? We are only explaining the obscure by the more obscure in thus reasoning. It is perfectly plain that double exchanging can never be continually taking place between molecules unless the heats of combination are the same, and consequently anything that explains one will explain the other. I would rather look for an explanation of both in the direction I have already pointed towards as to the dependence of the forces between molecules upon their distance apart and on the way these and their internal energy are all bound together by the conditions of temperature equilibrium. The question is evidently in the highest degree complicated, and for a complete discussion must introduce the theory as to the nature of temperature equilibrium, and in the meanwhile it is misleading to pretend that a matter is simple which is in reality most obscure by speaking of acknowledged analogies as if they really explained anything.

It may be of interest to remark in connection with the question of the chinks within which molecules move that very rough estimate can be made as to their size by considering the crude hypothesis that each ion is moved by the electric force near it acting on its ionic charge, and by calculating how long it would be in getting up its ionic velocity. Assuming that the ion moves like a body in a viscous liquid, the time it takes to get up its velocity must be a very small part of the time during which a current acts on it, and for which it obeys Ohm's law, because, for this to hold, the velocity must be independent of the time during which the current is acting. By some rough estimates as to the quantities involved it appears that the time during which an atom is acquiring its ionic velocity is somewhere about 10^{-10} of a second, and that the space it would acquire it in is about 10^{-20} of a centimetre. This seems as if the intermolecular bombardment distances were probably very small, and it shows that we can hardly expect Ohm's law to fail for electrolytes due

* Professor J. Emerson Reynolds informs me that such redistributions are recognised as occurring in complex molecules.

to this cause until the rate of alternation of our current is comparable with that of light. Of course the actual jostling of an atom through the molecules can hardly be fairly represented by such a crude hypothesis as that it is like a body moving in a viscous fluid; yet such a calculation as the above may be of use in showing the sort of quantities we may have to deal with.

Professor OLIVER LODGE said he had not been closely attending to these subjects during the past year or two, and accordingly only made a very few remarks, mainly with reference to the views he formerly expressed.

He had always endeavoured to moderate between the extreme dissociation views on the one hand, and those which require the molecule to be electrolytically torn asunder on the other. One reconciling fact is the chemically proved fact of double decomposition whenever two substances are mixed; this seemed to him to establish clearly that molecules are accustomed to interchange their atoms. Now, during the moment of interchange there is an instant of freedom, an instant of potential dissociation, and it is upon this that he had looked as the opportunity demanded by electric force to cause a slight diversion, sufficient in the long run to result in opposite atomic processions.

But, as Fitzgerald has somewhere pointed out, an infinitesimal moment of time is not sufficient to permit any finite effect, unless the forces acting are enormous, which in the middle of the liquid they certainly are not. This is therefore a difficulty, for if the atoms are solitary for any reasonable time, that amounts at once to actual dissociation, as postulated by Clausius. One may have to fall back, therefore, on the outlying atom stragglers from gross complex molecules as giving the necessary pseudo-freedom or potential dissociation which is all that Ohm's law and electrolytic facts demand, if one is to avoid admitting that extreme state of dissociation which physically seems to be so satisfactory and chemically so abhorrent.

But on this head it seems that no logical argument definitely asserting this latter view has been adduced. The fact that solutions do, in many respects, as shown by their osmotic pressure for instance, obey gaseous laws, is of high interest; but to argue from it that therefore their atoms must be in the same state of independent freedom as the atoms of a gas, is to commit the fallacy called by logicians "the illicit process of the major."

Moreover it is not quite apparent why (in Mr. Pickering's paper, for instance) the antithesis of the hydrate theory is supposed to be the dissociation theory. Free molecules in solution, rather than free atoms, would seem to be the opposite to the formation of definite chemical hydrates.

Lastly he hoped he might be permitted one more word on the subject of an old communication by Professor Ostwald relating a hypothetical experiment on statically electrifying an electrolyte, which he controverted some year or two ago, and which has been referred to by Mr. Pickering as if it were equivalent to a perpetual-motion device. He wished to dissociate himself entirely from Mr. Pickering's position on this point, and to explain what he had not yet had a good opportunity for explaining, that his published hostile remarks were made at first with the idea that the experiment was related as an experiment, and subsequently with the view that it is not very safe to use hypothetical experiments as controversial weapons. The view held by Professor Ostwald, that an electrolyte charged positively is so charged by reason of its hydrogen atoms looking outwards, while if charged negatively its oxygen atoms look outwards, is an extremely probable and instructive mode of regarding the matter. But an experiment establishing the truth of this view would have no necessary bearing on the dissociation controversy; in other words, the experiment suggested by Professor Ostwald, even if it could be performed, would not be a crucial one. The accepted laws of electrolysis already enable one to say what will happen when the minute

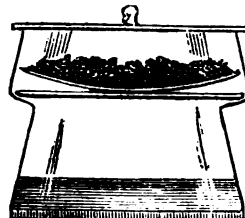
current of a displaced electrostatic charge is passed through a liquid, with as much clearness as one can say what happens when a battery is applied to it. There is really no difference between the two cases, except the presence or absence of electrodes; for, as Professor Fitzgerald has said, the facing-out atoms exist in each case, only in one they face the electrodes, and in the other they face the air.

(To be continued).

IS SULPHURIC HYDRATE VOLATILE AT THE ORDINARY TEMPERATURE OF THE AIR?*

By GEORGE A. KOENIG.

THE question proposed in the heading of this communication arose under the following circumstances. I had received a number of skeleton crystals of metallic iron which had formed in a steel block. To prevent them from rusting they had been coated with shellac. Previous to the analysis, the shellac was removed by alcohol, and after drying on water-bath, the material not needed for the purpose in view was placed upon a perfectly clean watch-glass into a desiccator of the common pattern. The watch-glass was supported by an iron wire triangle; its rims did not touch the sides of the desiccator. Upon the latter's bottom was pure sulphuric acid about one inch deep. The lid fitted with a film of vaseline. The desiccator was then placed upon a shelf and remained there undisturbed for about nine months. Being needed



for another purpose I took it down, and found to my astonishment that both the iron-wire triangle and the iron crystals were covered with a clean white crust. What could this crust be? My first supposition reverted to the nitrous compounds frequently found even in re-distilled sulphuric acid. The crust was very coherent and peeled off in scales, leaving a bright metallic surface. I noticed that those parts of triangle which had rested in immediate contact with the glass were not incrustated. Likewise the watch-glass was bright and free from dust. The crust dissolved readily in distilled water, and proved to be composed of *anhydrous ferrous sulphate*. The test for nitric and nitrous acid resulted negatively. A quantitative analysis was not made under the circumstances.

How was this ferrous sulphate formed? Two possibilities only seem to present themselves:—

a. The acid has crept up the side of the vessel, and also from the triangle along the watch-glass, by capillary force. This hypothesis is not well sustained. In the first place the sides proved themselves dry and clean, and so did the watch-glass. In the second place, one should expect the strongest action where the triangle rested on the glass. But the fact obtained that these contacts were not corroded.

b. The acid is volatile at ordinary temperature, similarly to other liquids with high boiling-point, such as mercury. It might even be proposed that this volatilisation is induced by the strong basic character of metallic

* Read at the Chemical Section of the Franklin Institute, January 20, 1891.

iron, and the minute quantities volatilised being immediately absorbed by the iron, there would not be any appreciable tension. There must have been produced, of course, a corresponding quantity of hydrogen, which would cause tension. I neglected to collect at once the gas in the desiccator, and a test was thus impossible. On the other hand, the lid was not so tight that such a thin gas could not readily escape.

There seems to me at present no escape from admitting the volatility of sulphuric hydrate at temperatures not exceeding 30° C., and more particularly in the presence of bodies exerting chemical attraction.

It will be probably of use to many to bear this fact in mind when they employ sulphuric acid as a desiccating medium. I propose to institute—and, in fact, have already instituted—several sets of conditions for proving or disproving this volatilisation. They will necessarily be time taking, as time seems the chief factor in the case.

NOTICES OF BOOKS.

Fresenius' Quantitative Analysis. Vol. II. Translated by C. E. GROVES, F.R.S. Part III.

THIS issue of the *magnum opus* of the great master of analytical chemistry includes the special part from §215 (acidimetry), to §245 (zinc-dust). We may safely say that it is a decided improvement on former editions. New methods and new precautions are given whenever necessary, and causes of error are pointed out whenever they have been detected.

In the directions for acidimetry, it is to be noted that the author, upon the whole, still prefers litmus to all other indicators, though he recognises that they may in certain cases have an advantage.

We remark that the translator, possibly in accordance with the wish of the author, retains a nomenclature which the majority of chemists have abandoned. He writes, *e.g.*, not sodium carbonate but carbonate of soda. No chemist, we feel sure, will willingly dispense with this standard book of laboratory reference, and we can only hope that it may soon reach its completion.

CORRESPONDENCE.

ATOMIC WEIGHTS.

To the Editor of the Chemical News.

SIR,—I have read the letter of "F.H.P.C." in the CHEMICAL NEWS (vol. lxiii., p. 130), in which he draws attention to the fact that in my little book, "The Analyst's Laboratory Companion," I have given "erroneous" atomic weights of platinum and osmium. The latter, as he justly remarks, is "less material to the analyst," but, as he goes on to state, "it is very desirable that the exact equivalent of such a reagent (*!*) as platinum should be used in calculating the results of our analyses." It certainly is eminently desirable that the practising analyst should use correct factors for calculating the results of his analyses, and it is for this very reason that, after much careful consideration, I finally adopted the value $Pt=197.2$, because this gives the most correct factors for calculating K_2PtCl_6 into K_2O , &c., and for converting the corresponding ammonio-compound into N , &c. In fact, when preparing the MS. of the work, the very first thing I did was to settle the matter of atomic weights in a manner that would commend itself to the analytical profession generally as indicated in my preface, and I went to a great deal of trouble in comparing the lists of atomic weights in a number of standard works

before making out my final list. I will now quote the authorities which determined me to take $Pt=197.2$.

1. In Crookes's "Select Methods of Chemical Analysis" (last edition), we read, regarding the estimation of potassium, that Messrs. Teschemacher and Smith's method gives results which are "very accurate." The authors take 244.2 as the equivalent of the potassium platino-chloride." I take 488.2, which, being almost exactly double, gives results that are practically identical when worked out consistently.

2. In Dittmar's "Exercises in Quantitative Chemical Analysis," p. 236, we are told that after drying the double chloride at 100°, $PtCl_6K_2 \times 0.30627$ (an empirical factor), $= KCl$, the author adding the following remark: "The factor 0.30707 calculated from (Seubert's) $Pt=194.8$, does not afford so close an approximation." Further back in the book we find (by Tatlock's method), $PtCl_6K_2 \times 0.1940$ (also an empirical factor), $= K_2O$. My factors are—

$$PtCl_4, 2KCl \times 0.19254 = K_2O.$$

$$" \quad \times 0.30520 = KCl.$$

3. Lunge and Hurter in their "Alkali Makers' Pocket Book," agree exactly with me in the above factors. Moreover, they expressly state in their preface that the atomic weight taken for platinum is "the figure adopted by all German potash manufacturers and analytical chemists."

4. Adriance, in his "Laboratory Calculations," adopts F. W. Clarke's list of atomic weights, with the single exception of platinum, on which he has the following note:—"It has been carefully determined that the atomic weight of platinum should be taken as 197.18, while really it is 194.1, since the factor obtained from 197.18 gives more correct results in calculations (*vide* Fresenius, *Zeit. für Anal. Chem.*, vol. xxi., 1882, p. 234)." Nevertheless, the factor he gives— $K_2PtCl_6 \times 0.30697 = KCl$ —is undoubtedly too high (see 2 above). In his more recent work "Chemical Arithmetic" Dittmar again supports me in my sets of factors for both the ammoniac and the potassic platino-chlorides. He takes $Pt=195.5$.

As regards osmium Clarke gives $Os=198.49$, Dittmar 191.5 in the work last named, but 195.0 in his former work; and "F.H.P.C." gives 190.3. There are such wide divergences that the matter seems to me to require further elucidation. I took what seemed to me, and still seems to me, the most probable value.—I am, &c.,

A. E. JOHNSON.

20, Victoria Street, Wolverhampton,
March 17, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxii., No. 9, March 2, 1891.

On the Composition of Drainage Waters.—P. P. Dehérain.—The author continues his observations on the drainage waters from fields, which he finds vary excessively in different soils. Thus the nitric nitrogen found in the drainage of a hectare of land at Wardrecques (Pas de Calais), from March to November, 1890, was 152.4 kilos.; at Blaringhem (Nord), 128.1; at Marmillat (Puy de Dôme), 62.5, and at Palbost, in the same department, only 45.2. The black soils of the two last localities are much richer in organic matter than the light brown soils of the North. The researches of Warington and Winogradski have shown that an abundance of organic matter in a soil retards nitrification. Nitrification is useful in spring, and often requires to be supplemented by the use of Chilean nitre. An abundant nitrification in

autumn occasions considerable loss. To prevent this waste he proposes to sow vetches and colza immediately after harvest.

On Certain Alkaline Derivatives of Erythrite.—M. de Forcrand.—The author has obtained an anhydrous potassium erythrate and three new hydrates, as well as an anhydrous sodium erythrate, which may also be obtained by the action of erythrate upon sodium methyrate. The formula of the hydrates have not yet been determined.

On Cotton-Dyeing.—Leo Vignon.—This fibre shows very feeble chemical functions in comparison with animal fibres. The author inquires if the chemical inactivity of cotton is the cause, or the effect of its deficient aptitude for fixing colouring-matters? To decide this question he treats cotton in sealed tubes with an excess of aqueous ammonia or of ammonium-calcium chloride, at temperatures between 100° and 200°. The quantity of nitrogen thus taken up varied from 1.05 to 2.86 per cent. The samples became capable of absorbing considerable proportions of colouring matters, such as orange, roccelline, soluble rosaniline blues, &c.

On a Vegetable Hematine, Aspergilline—the Pigment of the Spores of *Aspergillus Niger*.—Georges Linoessier.—Aspergilline presents striking analogies with the hematine in blood. Both contain a notable quantity of the same metal, iron. Both furnish by the action of energetic reducers a product which is oxidised in contact with air, and thus returns to its original state.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. v., No. 2.

Essay on the Laws of Berthollet.—Albert Colson.—It is necessary either to preserve the laws of Berthollet, restricted, however, to the bases of the same order, as the author has done, or else add to the principle of maximum work other indispensable considerations as Berthelot has done. In the precipitation of aniline salts by pyridine the latter chemist considers that the decomposing action of water upon the salts of aniline must be admitted to intervene.

Oxidation Products of Dimethylaniline.—Ch. Lauth.—It is well known that dimethylaniline submitted to the action of certain oxidising agents yields Paris violet. The reaction is different if we take as oxidising agent lead dioxide. On adding PbO₂ to an acetic solution of dimethylaniline we obtain a very fine green colour, or an orange-yellow if the acid is in excess. Fischer has observed the formation of violet and of formic aldehyd by the reaction of MnO₂ upon dimethylaniline sulphate in a dilute aqueous solution.

Coloured Reactions of the Aromatic Amines.—Ch. Lauth.—Already noticed.

New Process for Determining Oxygen Dissolved in Water.—G. Linoessier.—This paper will be inserted in full.

Supplementary Paper on a Process for Identifying Free Chlorine, and on the Detection of Chlorides in Presence of Bromides and Iodides.—The author refers to a method for identifying free chlorine which appeared in the *Bulletin de la Soc. Chimique* for October 20th, 1890. For identifying chlorine he now proposes the reaction of aniline phenate indicated by Jacquemin. The reagent is prepared by dissolving in 1 litre of water, and without alcohol, 40 grms. of phenol and 5 c.c. of aniline. A few c.c. of this solution heated nearly to the boiling-point and then mixed with very small quantities of a hypochlorite, rendered strongly alkaline with soda, give at once a fine blue colouration.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. v., No. 60.

Contains a continuation of the researches of Sir J. B. Lawes and Dr. Gilbert, from the *Proc. Roy. Soc.*

MISCELLANEOUS.

Royal Institution of Great Britain.—The following are the probable arrangements for the Friday Evening Meetings after Easter, 1891:—

April 10th. Sir William Thomson, D.C.L., LL.D., Pres. R.S., "Electric and Magnetic Screening."

April 17th. Professor A. W. Rücker, M.A., F.R.S., "Magnetic Rocks."

April 24th. The Rev. Canon Ainger, M.A., LL.D. "Euphuism—Past and Present."

May 1st. James Edmund Harting, Esq., F.L.S. F.Z.S., "Hawks and Hawking."

May 8th. Professor W. Ramsay, Ph.D., F.R.S., "Liquids and Gases."

May 15th. Professor G. D. Liveing, M.A., F.R.S., "Crystallisation."

May 22nd. Professor J. A. Ewing, M.A., F.R.S., "The Molecular Process in Magnetic Induction."

May 29th. David Gill, Esq., LL.D., F.R.S., Her Majesty's Astronomer at the Cape of Good Hope, "An Astronomer's Work in a Modern Observatory."

June 5th. St. George J. Mivart, M.D., F.R.S.

June 12th. Professor Harold Dixon, M.A., F.R.S., "The Rate of Explosion in Gases."

The following are the lecture arrangements after Easter:—

Mr. J. Scott Keltie, three lectures on the "Geography of Africa, with special reference to the Exploration, Commercial Development, and Political Partition of the Continent"; Dr. E. E. Klein, three lectures on "Bacteria: their Nature and Functions" (the Tyndall Lectures); Mr. William Archer, four lectures on "Four Stages of Stage History (the Betterton, the Cibber, the Garrick, and the Kemble Periods)"; Professor Dewar, six lectures on "Recent Spectroscopic Investigations"; Dr. A. C. MacKenzie, four lectures on "The Orchestra considered in connection with the Development of the Overture"; Professor Silvanus P. Thompson, four lectures on "The Dynamo"; Mr. H. Graham Harris, three lectures on "The Artificial Production of Cold"; Professor A. H. Church, three lectures on the "Scientific Study of Decorative Colour."

Programme of the Société Batave de Philosophie Experimentale: a Rotterdam.—The Society proposes among others the following questions:—

9. *Question 154.*—The best and most economical method of heating large buildings, having in view the demands of hygiene.

10. *Question 155.*—An experimental research on the cause of phosphorescence, especially among animals of a lower order.

12. *Question 159.*—A new and very exact determination of the variability of the specific heat of mercury with reference to temperature.

14. *Question 164.*—An exact determination of the refraction indices of substances which are abnormally dispersive and determination of the absorption-spectrum of these substances and of the spectrum of the superficial colour which often appears in these substances.

16. *Question 166.*—An examination of the specific heat of rhombic sulphur above 100°; of monoclinic and amorphous sulphur at different temperatures; of red phosphorus above 100°, and of ordinary phosphorus at different temperatures.

21. *Question 176.*—Monographs of an element, e.g., sulphur; of a compound, e.g., carbon disulphide or quinine; in a class of compounds, e.g., the nitro-derivatives; on a phenomenon or a series of phenomena, e.g., the action of sulphuric or nitric acid upon other bodies.

22. *Question 177.*—Very careful experimental determinations of the atomic weight of at least one element which is not yet well known.

25. *Question 181.*—A description of the vital conditions

of one or more species of moulds, ferments, or bacteria, which are important in horticulture, agriculture, the manufacture of butter, cheese, beer, vinegar, &c., and the manner in which these organisms affect the practice of such branch of industry.

The prize offered for the best answer to any of these questions is the Society's gold medal of the weight of 30 ducats. The papers must be drawn up in Dutch, French, English, German, or Latin, legibly written in the italic character (a prudent reservation as excluding German script), not in the hand of the author, and marked with some motto. Each must be accompanied by a sealed paper bearing the same motto and containing the name and address of the author. They must be sent post free to the Chief Secretary, Dr. G. J. W. Bremer, on or before February 1st, 1892.

MEETINGS FOR THE WEEK.

THURSDAY, April 2nd.—Chemical, 8.
FRIDAY, 3rd.—Geologists' Association, 8.
Quekett, 8.

TO CORRESPONDENTS.

W. Naylor.—We know of no method of sterilising sewage.

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THE CHEMICAL NEWS.

VOL. LXIII., No. 1636.

BOGUS LETTERS.

THE anxiously-awaited Anniversary Meeting of the Chemical Society has been held. As was only to be expected, motions of which notice had not previously been given were ruled out of order by the chairman, and for this reason the section of the Society which is discontented with the present conditions under which Fellows are elected, can hardly be said to have had that opportunity for discussing what they consider to be their grievances which they probably hoped for.

Rumours of a special meeting were afloat later in the evening, and it is to be sincerely hoped that such may be held, for it is obviously unhealthy to have a fermentation in our midst which cannot be properly ventilated.

But whether or not it be right that only such should be admitted to the Chemical Society as have taken an active part in the advancement or practice of the science, certain it is that prompt steps should be taken to prevent those who are not Fellows of the Society from using the letters F.C.S. It is therefore a matter for congratulation that the President was able to announce that steps were being taken, in conjunction with the Royal Society and other learned societies, for the introduction of a Bill in Parliament to render such fraud punishable.

Unfortunately, the system of Government under which this country labours renders the passing of a Private Bill a slow and tedious process. Meantime the wicked flourish like a green bay tree, and weekly advertisements appear in which the advertisers allege that they are "F.C.S."

Under these circumstances, the Chemical Society might do much for itself. Whenever it becomes known that any person is using these letters when he has no right to do so, let the Society publish far and wide the fact that he is not a Fellow. Of course, an immediate objection will be made to this suggestion: that such a course would merely serve to advertise the advertiser, and would do no real good; but this objection is not valid if the assertion that the public believe the letters F.C.S. to have a professional value be adopted, and we have good reason for supposing that this view is generally accepted.

We have pointed out what we believe to be an easy way of preventing that which is becoming a very serious fraud, not only upon the public, but upon the chemical profession. If it is adopted, we shall expect to see the bogus letters after the names of so-called analysts rapidly disappear.

ON THE INFLUENCE OF PRESSURE ON THE SPECTRA OF FLAMES.*

By G. D. LIVEING, M.A., F.R.S., Professor of Chemistry, and J. DEWAR, M.A., F.R.S., Jacksonian Professor, University of Cambridge.

(Concluded from p. 145).

Oxy-hydrogen Jet in Carbonic Acid Gas.

For this experiment a two-branched tube (the upper one in the figure) was used. The jet of mixed oxygen and hydrogen was first lighted and introduced into the experimental cylinder while the latter was full of air and the stopcock *s* open. The air was then replaced by CO₂ entering by the tube *c*. The effect of this was at once to brighten the flame and change its colour from yellow to

blue. Seen in the spectroscopic, the change consisted in an increase of continuous spectrum, especially towards the more refrangible end. When the stopcock *s* was closed so that the pressure rose in the experimental cylinder, the flame increased in brightness, but there was no other change in the spectrum. It remained continuous with no bright or dark lines, or bands, except the D lines of sodium. It resembled an ordinary flame of CO. The jet would not burn in CO₂ unless there was some excess of oxygen, and even with an excess of oxygen we could not get it to continue to burn in CO₂ at a pressure higher than two atmospheres.

Ethylene in Oxygen.

A jet of ethylene burning in oxygen gave, when the flame was small, the usual candle-flame spectrum, together with a band in the indigo (λ 431) shading towards the violet; but as the pressure was increased, the continuous spectrum brightened and completely overpowered the bands, and at the same time the absorption spectrum of NO₂ appeared. We carried the pressure up to 33 atmospheres, and at that pressure the flame seemed to give nothing but a continuous spectrum, intersected by the absorption bands of NO₂. In our tube the flame was viewed almost directly end on, and it is possible that if we had seen the flame sideways we might have detected the hydrocarbon flame spectrum near the nozzle. At the high pressure much soot separated. We tried burning a mixture of ethylene and oxygen. The mixed jet burnt well in air, and when the supply of oxygen was sufficient, gave the hydrocarbon flame spectrum. In the experimental tube in oxygen, the jet burnt well at the atmospheric pressure, but we failed to get it to continue burning when the pressure was increased. The shaded band, commencing with a sharply defined edge about λ 431, seems to be independent of the pressure, and has been before observed in a gas flame (Huggins, *Proc. Roy. Soc.*, vol. xxx., p. 580). In fact, the only effect of pressure in this, as in the former cases, seemed to be the increase of the continuous spectrum.

Cyanogen and Oxygen.

As we could not obtain cyanogen at such pressures as we had used in the case of the other gases, we were obliged to content ourselves with exploding mixtures of cyanogen and oxygen in an iron bottle, fitted with a quartz stopper like that of the experimental tube above described. The bottle, having been exhausted by an air-pump, was filled with the mixture of gases, and exploded by an electric spark. With less than 3 vols. of oxygen to 1 vol. of cyanogen, there was always a considerable deposit of carbon, which covered the quartz and impeded vision; but, with 3 vols. of oxygen to 1 of cyanogen, the carbon was all burnt. Notwithstanding the brilliant banded spectrum of a flame of cyanogen in oxygen at ordinary pressure, nothing but a continuous spectrum could be seen in the flash of the exploded gases, except the ubiquitous D lines of sodium. The continuous spectrum was bright. Photographs showed a continuous spectrum with lines of iron, calcium, potassium, and sodium, but no cyanogen or carbon bands, or carbon lines. When a little hydrogen was added to the mixture of gases, no trace of the hydrogen red or green line could be detected in the spectrum of the exploding gas.

In every case, the prominent feature of the light emitted by flames at high pressure appears to be a strong continuous spectrum. There is not the slightest indication that this continuous spectrum is produced by the widening of the lines, or obliteration of the inequalities, of the discontinuous spectra produced by the same gases at lower pressures. On the contrary, it seems to be developed independently. This is, on the whole, quite in accordance with what would be expected, considering that under pressure the molecules of the gases have much less freedom, encounters amongst them are much more frequent, and they have much less chance

* Abstract of a Paper read before the Royal Society, Feb. 19, 1891.

of vibrating independently, and of taking up exclusively, or chiefly, the fundamental rates of vibration which are natural to them when free. Their condition, during a large part of any given time, approximates to that of the molecules of a liquid, and their spectra approximate to that of a liquid to at least a like extent. On the other hand, the higher temperature which, in many flames, attends an increased pressure ought to give some intensity to the special radiation which the molecules emit during their time of free motion; and this we have noticed to occur in the principal sections of the discontinuous spectrum of the oxy-hydrogen flame. Whether the continuous spectrum is due to the mutual action of the molecules of the compressed gases may perhaps be best determined by some photometric measures of the rate at which the brilliance increases with the pressure. Frankland ("Experimental Researches," pp. 892 *et seq.*) has made some such measures, but not sufficient to solve the question. We have made an attempt to measure, not the total intensity of the light, but that of rays of definite refrangibility.

Photometry of Oxy-Hydrogen Flame under Pressure.

The apparatus used for these measures was a spectro-photometer of the pattern employed by Crova (*Annales de Chimie*, series 5, vol. xxix., p. 556). In this, the rays of one of the sources of light to be compared are passed through two Nicol's prisms, and then reflected into one half of the slit of the spectroscope, while the light from the other source passes directly into the other half of the slit. By turning one of the Nicol prisms, the light from the first source can be reduced at pleasure, and any small section of the spectrum can be separately observed by cutting off the rest by means of a shutter in the eye-piece. We found it by no means easy to get good concordant observations. A much larger vessel was used than for the earlier experiments, one which contained several litres, and so we may presume a more uniform pressure was maintained within it. The results of the best series of observations on the photometric intensity of the jet of oxygen burning in hydrogen are given in the following table. The comparison light was a petroleum lamp.

I.	II.	III.	IV.
15 lbs.	3°	274	$30 \times 3^2 = 270$
35 "	7	1485	$30 \times 7^2 = 1470$
55 "	11	3641	$30 \times 11^2 = 3630$
75 "	14	5853	$26 \times 15^2 = 5850$
95 "	19	10600	$29 \times 19^2 = 10469$

The first column gives the pressure of the gas, the second the mean of four to six observations of the angular deviation of the Nicol's prisms from the position of complete extinction for each pressure. The third column gives the squares of the sines of the angles in the second column multiplied by 100,000.

It will be seen from the last column that the numbers in the third column, which should be proportional to the photometric intensities at the respective pressures, are approximately proportional to the squares of the pressures.

This may be taken to indicate that the brightness of the continuous spectrum depends mainly on the mutual action of the molecules of gas.

A series of similar observations on hydrogen burning in oxygen gave somewhat different results, tabulated below:—

I.	II.	III.
15 lbs.	6°	1093
35 "	13	5060
55 "	18	9549
75 "	22	14033
95 "	28	17861

The flame was brighter than that of oxygen burning in hydrogen at ordinary pressure, but the rate of increase with increased pressure was not so rapid as in the former

case. It seems as if the continuous spectrum were made up of two parts, one varying as the square of the pressure and another according to some other law. The flame is evidently not the same in the two cases. The products of combustion derived from the small quantity of air are different, and also the hydrogen jet always showed the presence of sodium, sometimes calcium. The appearance of the flame was also different; the hydrogen jet being faintly visible and yellowish in the elongated part, whereas the light from the oxygen jet was concentrated near the base, the point being invisible. The measures of which the means are tabulated above were also less concordant than the corresponding measures for the oxygen jet. We were unable to carry our measures beyond a pressure of 95 lbs., because at higher pressures a cloud was formed in the apparatus which prevented our seeing the flame directly. We hope to prosecute these measures with flames of other gases, and, if possible, at higher pressures.

The conclusions to which our experiments have led seem inconsistent with these which have been drawn from Plücker and Hittorf's well-known observations on the widening of the hydrogen lines in vacuous tubes with a residue of hydrogen when that residue increases. That the widening of the lines in a Plücker's tube results from increasing the density of the residue of hydrogen in the tube cannot be gainsaid, but we are wholly ignorant of the mechanism by which the gas is lighted up by the electric discharge. It is sometimes assumed, but without any sufficient reason, that the energy of the electric current is first converted into heat, and then in turn into radiation; but the electric energy may equally well be directly converted into the motion of radiation. As a fact, we have never yet been able to obtain either the emission or the absorption spectrum of hydrogen without the aid of an electric current, so that, in reasoning on this spectrum, we are much more in a region of speculation than when treating of flames. Whether the hydrogen lines, bright or dark, in the solar spectrum are produced directly by the high temperature of the sun, may even be called in question. And though we may admit that the density of the hydrogen in the sun's atmosphere, outside the photosphere, is but slight, it does not follow that the total pressure of all the gases forming that atmosphere is so very small as Messrs. Frankland and Lockyer (*Proc. Roy. Soc.*, vol. xvii., p. 288) have, from the width of the lines, concluded it to be. After all, it is not so easy to connect the temperature, even of a flame, with its radiation, for it is only when the condition of a gas is steady that we can assume that there is a definite relation between the motion of agitation, on which temperature depends, and the vibratory motions, on which radiation depends. In speculating on such questions, chemical, as well as electrical, changes must not be lost sight of, although the latter may be more directly concerned in radiation.

Experiments which we have commenced upon the arc in an atmosphere of compressed gas tend to the same conclusion. It does not appear that the metallic lines in the arc are sensibly affected by a steady pressure up to 15 atmospheres. The details of these observations, which are complicated by the variation of resistance with change of pressure, we defer until the experiments are finished.

On the Ptomaines.—M. Oechsner de Coninck.—A completion of the study of the ptomaine $C_{10}H_{15}N$. Its iodomethylate was dissolved in absolute alcohol; to the solution whilst still hot there was added a single drop of strong potassa lye. A bright red colouration appears at once and soon turns brown. The dark liquid in about an hour presents a blueish-green fluorescence which lasts a long time. The two ptomaines, $C_8H_{11}N$ and $C_{10}H_{15}N$, certainly belong to the pyridic series, but are not hydrides.—*Comptes Rendus*, vol. cxii., No. 11.

ON THE BISULPHITE COMPOUNDS OF
ALIZARIN-BLUE AND CÆRULIN AS
SENSITISERS FOR RAYS OF
LOW REFRACTIBILITY.*

By GEORGE HIGGS.

THE determination of the relative wave-lengths of the Fraunhofer lines, by photographing all the orders of spectra given by any particular grating, includes certain subjects which present more or less difficulty, and that of selecting or producing a dye-bath adapted to the requirements of the two or more orders comprising the subject is intimately connected with that of the choice of absorbing media.

Having been engaged for some time in investigations of this nature, I had occasion, during the summer of 1889, to require an impression of the 2nd order, about w.l. 3300, contiguous with that of the red end of the 1st order, and finding that the ordinate of an actinic curve for a plate immersed in a very dilute alcoholic ammoniacal solution of cyanin (1:30,000), reduced to about one-fourth of that for an unprepared plate, I abandoned its use for this purpose. The results appeared to be unaffected by the addition of quinine.

Subsequently, induline, cœrulin, alizarin-blue, and the bisulphite compounds of the two latter were used, and when obtained in a state of sufficient purity the alizarin-blue S leaves little or nothing to be desired, for, whilst possessing, in a high degree, sensitising properties for rays throughout the region comprised between w.l. 6200 and 8000, it does not, as in the case of cyanin, lower the sensitiveness to the violet and ultra-violet.

The following is one of the processes I employed in the preparation of the dye-stuff in a pure state:—

To a saturated solution of sodium bisulphite in a mortar is added alizarin-blue paste, disintegrated with a pestle, and poured into a glass vessel capable of holding an additional quantity of sodium bisulphite, in all 10 parts of the paste to 20 parts of bisulphite, and another 10 parts of water. The vessel is well stoppered, set aside in a cool place for five or six weeks, and shaken daily, but left undisturbed during the last eight or ten days.

The solution is decanted, filtered, and treated with alcohol, to precipitate the greater portion of the remaining sodium bisulphite. 50 parts of water are now added with a sufficiency of sodium chloride to form a concentrated solution. Again set aside in an open-mouthed glass jar, covered with bibulous paper, for seven or eight days, a deposition of the dye in a crystalline state, together with sulphite of calcium, will take place, which latter, owing to its insolubility in water, may be removed by filtration.

The alizarin-blue S is separated from any unaltered substance left in the original stoppered vessel by solution, and added to the brine, now purified from lime salts, and once more set aside to crystallise, the final purification being effected in a beaker containing alcohol and a small percentage of water to remove the last traces of sodium chloride, collecting the crystals on a filter-paper and drying at ordinary temperatures.

The needle-shaped crystals are of a deep red. Dilute solutions are of a pale sherry colour, changing, with the addition of a few drops of ammonia, to a green, which immediately gives way to magenta and every shade of purple, till oxidation is complete, when it assumes a blue colour, the absorption spectrum of which is continuous and strongest in the least refrangible end, presenting the appearance of extending into the infra-red.

Plates immersed in a solution containing 1:10,000 and 1 per cent of ammonia give the most perfect results the day after preparation, but rapidly deteriorate unless kept quite dry.

With a slit $\frac{1}{1000}$ inch in width, and an exposure of forty

minutes, results have been obtained in the region of Great A of the 2nd order, which possess all the detail and definition usually so characteristic of the violet end. Numerous lines are sharply depicted which were previously not known to exist. W.l. 8400 has been reached, giving almost equal detail.

The process for the preparation of pure cœrulin S is a slight modification of the preceding. The results obtained, as well as the actinic curve, are almost identical. The pure substance is almost white; dilute solutions pass rapidly from pale yellow to a bright green; a trace of ammonia produces an olive-green.

For several samples of paste I am indebted to the kindness of Messrs. Schott, Segner, and Co., of Manchester, agents to the Badische Anilin- und Soda-Fabrik, Ludwigshafen, who hold the patent rights for the manufacture of alizarin-blue S. It is hoped this company may be induced to manufacture this substance free from the minute crystallisable impurities which render it unsuitable for use in investigations of such delicate nature.

DISCUSSION ON THE THEORY OF
SOLUTION.*

(Continued from p. 151).

PROFESSOR OSTWALD read the following communication "On the Electrical Behaviour of Semipermeable Membranes":—

If we fill two glass beakers with copper sulphate solution, put in them two copper wires connected with a couple of Leclanché cells, and a galvanoscope, and close the circuit by a siphon filled with any electrolyte, which is prevented from mixing with the copper sulphate by covering the ends of the siphon with parchment paper, no phenomenon of special interest is to be noticed. We have an electrolytic circuit without polarisation, as used by Paalzow for the determination of the specific conductivities of liquids. By varying the liquid in the siphon only the total resistance of the circuit varies, and polarisation does not generally occur. If we fill the siphon with potassium ferrocyanide, nothing novel seems to go on at the first glance. But if we remember that on the contact of copper salts with ferrocyanides a *semipermeable membrane* of copper ferrocyanide is formed, through which, according to the observations of Traube, no copper salt can diffuse, we are led to a somewhat strange question. The fact that no copper salt can pass through the membrane is evidence that the copper ions existing in the salt solution are likewise unable to pass. But as the electricity in electrolytes travels only with the ponderable ions, we are met by the alternative either that the refusal of the copper (and ferrocyanide) ions to pass through the membrane will cause the current wholly to stop, or that the electricity will deposit the copper ions on the membrane and itself alone pass through. The semipermeable membrane must in the first case act as an *insulator*; in the second case it must act as a *metallic diaphragm*. Both these cases are so unexpected that the described experiment at once acquires a special interest.

By performing the experiment we find that the second alternative holds good. The current becomes rapidly weaker, and after ten minutes we can easily observe a very marked polarisation current in inverse direction to the primary current. After some hours of current the parchment paper containing the semipermeable membrane on the positive side is coated with a layer of metallic copper, and this is evidence that the copper ions are *filtered off by the semipermeable membrane*.

From this experiment it follows that the semipermeable membrane really acts as a sieve, not only as regards compounds, but also for ions, allowing some of them to pass

* Read before the Royal Society, March 12, 1891.

* British Association (Section B), Leeds Meeting, 1890.

and retaining others; for we know, for example, that potassium chloride can pass the membrane of copper prussiate, and therefore the ions K and Cl do so, while barium chloride and potassium ferrocyanide are retained. In the two last-mentioned cases one of the ions has the power of passing, but is retained by the other. At the first moment the Cl ions of the barium chloride will of course go through the membrane, while the barium ions stay behind. But by this separation a separation of positive and negative electricity also takes place, and thereby forces will arise tending to draw the Cl ions back. Finally a double layer of electricity is formed, causing a potential difference on both sides of the membrane, whose value depends only upon the molecular concentration of the electrolyte, and in no way upon its nature.

If the formation of the double layer is prevented, free diffusion of the passing ion takes place. By adding to the barium chloride some salt whose metal can pass through the membrane—for instance, some salt of potassium—the Cl ions at once will traverse the membrane, but the same number of K ions must go along with them. In this case, however, it may be assumed that the added potassium salt undergoes a double decomposition with the barium chloride, forming potassium chloride, which is able to diffuse through the membrane. But we can also cause the Cl ions to pass by putting some diffusible negative ions on the *outside* of the membrane—for instance, copper nitrate. Then we soon find chlorine outside and a nitrate inside the membrane. In this case it is impossible to assume a double decomposition, because both the salts are separated by the membrane, which prevents the diffusion of the barium chloride, as well as of the copper nitrate, and the explanation, by taking into account free migrating ions, seems to be the only sufficient one.

The above-mentioned double layers and potential differences, occurring at semipermeable membranes, when one of the ions of the electrolyte is retained, are probably the source of the potential differences and currents we meet with in living matter, because the cells of organisms are all coated with such semipermeable membranes. It is perhaps not too rash to hope that the ancient mystery of electrical fishes will find its solution on these lines.

Referring to the discussion Professor OSTWALD said—Professor Fitzgerald has asked why the ions, when they are free, do not separate by diffusion. The answer is that they do. If we have a solution of HCl, for example, consisting to a great extent of H and Cl ions, in contact with pure water, the H ions, moving much faster than the Cl ions, take the lead in wandering into the water. But a separation of electricity hereby takes place, and every ion being charged with a great amount of either positive or negative electricity, the electrostatic forces resulting from the initial separation soon prevent further separation. Therefore water must take a positive potential against a solution of hydrogen chloride, and in general water must show against every electrolytic solution the potential of the faster ion.

These considerations, which lead to the whole theory of the potential differences between electrolytes, were first developed by W. Nernst (*Zeitsch. f. phys. Chem.*, ii., 613, and iv., 129), who has confirmed them by various experiments; and further by M. Planck (*Wied. Ann.*, xl., 561). As far as I am aware, no theory of fluid-cells (*Flüssigkeitsketten*) had hitherto existed, and the possibility of developing one consistent with experiment from the principles first stated by Arrhenius is strong evidence in favour of his views.

Secondly, Professor Fitzgerald seeks for the source of energy required for the separation of, e.g., Cl and H by dissolving HCl in water. This question is in accordance with the widely-spread assumption that a great expenditure of work must be done to effect this separation. As a great amount of heat is developed by forming HCl from its elements it seems evident that the same amount of energy must be restored to the elements in separating

them. This is quite true if common hydrogen and chlorine were formed, but the ions H and Cl, existing in the aqueous solution of hydrogen chloride, are by no means identical with the so-called free elements. To use a word to which chemists are accustomed, the ions H and Cl are *allotropic forms* of these elements, similar to yellow and red phosphorus, and contain very different amounts of energy from those which they contain in their common state of hydrogen and chlorine gases. Therefore it is impossible to say anything *a priori* about the evolution or absorption of energy connected with the change from HCl gas to positively charged H ions and negatively charged Cl ions; we must interrogate facts; and these teach us that the ions generally contain much less energy than the elements in the common state, and therefore a great amount of energy is not called for in the transformation of, e.g., HCl into the free ions H and Cl.

The elements in the state of ions being charged with great amounts of electricity, the very different tendency of the elements to assume the state of ions can be conveniently called their different affinity for electricity. This expression is of course only a *façon de parler*, but it gives a good description of the behaviour of the elements. The action, for example, of zinc on cupric sulphate solution, containing the ions Cu and SO₄, depends on the greater tendency of the zinc to form ions; therefore the zinc tears the positive electricity necessary for its existence as an ion from the copper ions, and deposits the latter as unelectrical, i.e., common metallic copper. The SO₄ ions, being no closer connected with the zinc than with the copper, act only as, owing to their negative charges, they render possible the existence of an equal number of positive ions, no matter of what nature.

If I am right Professor Fitzgerald is now ready to acknowledge the views of Arrhenius as *possible* ones, but he assumes that the facts explained by these views can also be explained by some other views, of which he has given some specimens. It is, of course, impossible to deny this. But as the theory of Arrhenius has done its work up to the present, and the new theory has yet its way to make, the former seems to have certain claims to be preferred. As the theory of Arrhenius has shown itself to be consistent with a very great number of facts, in the most various branches of physics and chemistry, the new theory must of necessity lead in all these cases to the same result as that of Arrhenius. Then the scientific world will have the wonderful spectacle of two theories, starting from different points of view, but leading everywhere to the same result. Science will then possess a twofold means of further investigation of some of its most difficult problems; a state of matters that cannot be too urgently wished for by all who have devoted their powers to such investigations.

In reply to Mr. Pickering's remark that the induction experiment upon electrolytic solutions described by me is opposed to the first principles of science, especially to the first law of thermodynamics, I wish only to remind him that by carrying out the common lecture experiment with two metallic balls and a charged body, we can get from the balls a spark, and therefore also an amount of energy. As no one hitherto has found in this experiment a contradiction to the law of the conservation of energy, I can leave the defence of my experiment to all teachers who annually perform this experiment in their lectures.

Professor Lodge has asked if the experiment in question has been carried out, and in what manner. The description of a series of such experiments has been given in the *Zeitschr. f. phys. Chem.*, iii., 1889, p. 120. The easiest way to demonstrate the liberation of ions in electrolytes by induction is to fill a glass jar covered on the outside with tinfoil with dilute sulphuric acid, to connect the outside with a source of positive electricity, and to insert in the sulphuric acid an earth-connected capillary electrode, i.e., a short Lippmann electrometer. The very minute bubbles of hydrogen developed by electrostatical actions can then easily be observed in the capillary tube

on the boundary of the mercury and the sulphuric acid by help of a microscope.

Professor Armstrong has declared that the dissociation theory of electrolytes is unacceptable to chemists. As far as I am aware, there exists nowhere a real contradiction between chemical facts and the dissociation theory, but this theory only runs against all the time-honoured feelings of chemists. As feelings, although very powerful things, are at least variable with time and custom, it is to be expected that they will change sooner or later. The time is not very long past when the assumption that, in the vapour of ammonium chloride, hydrochloric acid and ammonia, which have "so great an affinity for each other," should exist separate from one another ran in quite the same manner against the feelings of chemists. Now we are accustomed to this conception, and in the same manner chemists will speak in a year or two as quietly of the free ions as they now speak of the uncombined mixture of hydrochloric acid and ammonia in the gaseous state.

But it should not be forgotten that a great many purely chemical facts—in the first place the great generality and regularity of the chemical reactions of electrolytes as used in analytical chemistry, in opposition to the variability and irregularity of the behaviour of non-electrolytes, especially of organic bodies—have found their first explanation in the theory of electrolytic dissociation. The objection against this theory, that if the ions of salts exist in a free state this would not be any ground for the law of constant proportion between acid ions and metals, is easily refuted. For, according to Faraday's law, all chemically equivalent amounts of positive and negative ions are charged with equal amounts of electricity; in an electrically neutral solution, as all ordinary solutions are, there cannot but exist an exact equivalent number of positive and negative ions. We see, therefore, the law of Faraday connected in the closest manner with Richter's law of chemical equivalents; if the one holds good, the other must also hold good, and *vice versa*.

Professor Armstrong has asked why water does not split into ions, while hydrogen chloride, a body similar to water, does. But has Professor Armstrong forgotten that liquid hydrogen chloride, like pure water, is an *insulator* for the electric current, as was found long ago by Gore, an observation afterwards confirmed by Bleekrode? It has been stated by F. Kohlrausch that at ordinary temperatures no pure liquid is a good electrolyte. The theory of Arrhenius is still in this point the only one which explains this strange fact; pure liquids do not conduct, because their molecules have no space to resolve themselves into ions.

It is therefore not improbable that water would conduct electrolytically if we could find a suitable solvent for it. An investigation in this direction would be of very great interest, but not without grave difficulties.

To a certain, but very small extent, water too contains ions, namely, H and OH. This is shown by the hydrolytic action of water on the salts of weak acids and bases, the amount of H or OH ions dissociated from these acids or bases being in such cases comparable with the amount of the same ions in water. Then the latter acts as a very weak acid or base, and the action follows the common law of masses, as J. Walker has shown (*Zeitsch. f. phys. Chem.*, iv., 319).

(To be continued).

STUDIES ON THE EARTHS OF THE CERIUM AND YTTRIUM GROUP.*

By A. BETTENDORFF.

THE material for the following researches was orthite, obtained from the establishments of Dr. Marquart, of Bonn, and Dr. Schuchardt, of Goerlitz, and said to have

* From *Liebigs Annalen*

been derived from Strömboe, near Arendal, and from Hitteroë. From the analysis of Angström and Clève, it appears that all the orthites contain varying quantities of the earths of the cerium and yttrium groups, in which considerable quantities of thorium are also present.

The rare earths of the orthite were separated according to the known methods which are also used for the decomposition of cerite. To remove the cerium and thorium oxide, the author used the process given by Debraye (*Comptes Rendus*, xcvi., 828). The nitrates of the earths are fused with six parts of potassium nitrate, a method which is expeditious and gives excellent results. The cerium compound is so completely removed that on treating the hydroxides of the earths with chlorine gas no trace can be discovered. On the other hand, very small quantities only of the other earths remain in the cerium oxide. After the removal of this oxide and of thorium, the earths of both groups are separated by means of potassium sulphate.

This separation has hitherto been effected exclusively by Mosander's method. The author has introduced a modification which has an influence upon the complete separation of the two groups. The cerium group contains certain oxides, the double potassium sulphates of which are only precipitated from a saturated solution of potassium sulphate very slowly and on vigorous agitation. The separation is therefore undertaken by preference in corked bottles which are filled with a solution of potassium sulphate, saturated when hot, and allowed to cool. The bottom of the bottle is then coated with a firmly adherent saline crust. If the separation is to take place without shaking, the bottle, after the introduction of the chlorides or nitrates of the earths, is completely filled with the saturated solution of potassium sulphate, corked up, and inverted; these are the conditions prescribed by Mosander. In the other case, the bottles are only filled partially. When both the groups have been separated, and the earths have been set free from the double sulphates, the separation of the two constituents is commenced.

The author has used the method of the partial decomposition of the nitrates, as it permits larger quantities to be worked up in a relatively short time. It is easily practicable to melt up the nitrates of the yttrium earths to a clear liquid, as their point of fusion is low and remote from their decomposition heat. Small quantities of the nitrates of the cerium earths can also be melted to a transparent liquid in a platinum crucible on an open fire. But if we attempt to operate on larger quantities, it appears that long before complete fusion is effected a part of the mass is decomposed, with separation of oxide and basic nitrate. Under these conditions the access of heat is not in harmony with the thermic conductivity of the solid nitrate, whence the portions lying nearest to the fire are melted and decomposed before the entire mass enters into fusion. This defect may be remedied by placing the platinum crucible containing the nitrates in a porcelain crucible in such a manner that there remains everywhere between the two an interval of from 1 to 2 m.m. As the porcelain crucible is very apt to crack, it is wrapped round with some rings of platinum wire, after which hundreds of fusions can be undertaken in it. In this manner large quantities of nitrate can be fused to a clear liquid, and, if heated more strongly, begin to decompose. As soon as small crystalline leaflets of basic nitrate appear on the surface of the melt, the contents of the crucible are poured into a large platinum capsule. The cold mass forms a perfectly clear solution in 10 parts of water; and, on boiling, basic nitrate separates from the solution in dense flocks, which are easily removed by filtration. From the concentrated filtrate a second separation is then obtained, and so further.

The earths, freed from cerium oxide and precipitable by potassium sulphate, after the last portions of the yttrium earths had been removed had an equivalent of $\text{RO} = 109.0$ to 110.2 . It is readily practicable to remove all lanthanum by systematic fractional precipitation of the nitrates of

these oxides. Small quantities of didymium oxide are still present, but the product has a high degree of purity, as is proved by the equivalent of the oxide $RO = 108.76$.

The separation is carried so far that in the basic nitrates ultimately obtained no lanthanum lines can be obtained in the spark-spectrum of the chloride. The united basic nitrates, when completely freed from La , furnish a brown oxide with the equivalent of $RO = 113.2$ to 114.0 . They contain all the didymia and samaria bands, larger or smaller quantities of gadolinia or terbia, according as the separation of the yttrium earths by means of potassium sulphate has been effected by Mosander's process, or by the modification above described.

The author now communicates the observations made whilst obtaining pure lanthanum compounds from the above-mentioned mixtures $RO = 108.76$.

A further purification by a systematic fractionated decomposition of the nitrates on fusion presents serious difficulties. Though the melting-point has become rather high, it is practicable, by the process above described, to obtain a clear melt from which leaflets of basic nitrate separate; but, on cooling, the congealed mass is scattered about as dust—the more, the richer it is in lanthanum nitrate—sometimes with such force that considerable quantities are lost. This phenomenon was observed by Berzelius, and is described in his "Lehrbuch."

It is more advantageous to apply the method described by Auer von Welsbach, which depends on the circumstance that in a solution of the mixed didymium and lanthanum-ammonium nitrates, the double salt of lanthanum first crystallises out, being much less soluble. Auer von Welsbach conducts this separation in a strong nitric solution. The author—as his preparation contained but little didymium—found it more convenient to allow crystallisation to take place in a solution as neutral as possible.

(To be continued).

MILK ANALYSIS BY THE ASBESTOS METHOD.*

By FRANK T. SHUTT, M.A., F.I.C., F.C.S.

To render complete the results of feeding experiments conducted at the Central Experimental Farm with thoroughbred stock, a comparatively large number of analyses of milk is required to be made. At the outset of this work, therefore, a process was sought by which the composition of the milk (*i.e.*, total solids and fat) could be accurately and rapidly ascertained.

After working Adams's, Wanklyn's, the plaster-of-paris, sand, and other methods, a trial was made of the asbestos method as described by Thomas Macfarlane, F.R.S.C., Chief Analyst, Department Inland Revenue, in a paper read before this Society in May, 1887. This process proved so satisfactory, both as to accuracy and rapidity, that I have been led to adopt it in the laboratory of the farm.

The object of this paper is to bring before your notice the results of some experiments contrasting this process with others in which (a) the total solids are estimated by evaporation in platinum dishes, and (b) in which the fat is determined by direct weighing in flasks after exhaustion of the milk solids in a Soxhlet tube. A series of experiments (the results of which are depicted in Table III.) was also undertaken to compare the percentages of fat obtained by the use of Soxhlet and Stutzer tubes respectively, the fat being estimated by difference. Lastly, as shown in Table IV., the results are given of a number of consecutive analyses, copied seriatim from the analyses book,

which show the degree of closeness with which duplicate assays can be made by the asbestos method, using the Stutzer tube for the extraction of the fat.

TABLE I.

T. solids by asbestos method.	T. solids by plat. dish.	Increase in percentage of t. solids by evap. in plat. dish.
12.85	13.25	0.40
14.36	14.73	0.37
15.21	15.70	0.49
12.80	13.14	0.34

First Column.—In these experiments, about 10 c.c. of milk was weighed in the tubes containing asbestos fibre, which had previously been dried in the steam cupboard.

The tubes, with the milk absorbed in the asbestos were then replaced in the steam cupboard, allowed to remain there twelve or sixteen hours (over night usually), cooled in the desiccator, and again weighed. The temperature of the cupboard during the operation of drying is between $85^{\circ}C.$ and $90^{\circ}C.$, a strong current of air passing through the chamber.

Second Column.—The milk, about 5 c.c., was weighed quickly into small platinum dishes. These were placed on a water-bath for four hours (the water being in brisk ebullition), cooled, and weighed. All the results are calculated from duplicate analyses.

It will be noticed from an inspection of the foregoing table that the solids obtained by drying in the platinum dishes are from 0.34 to 0.49 per cent higher than those obtained by the asbestos method. I am of opinion that the results from the former method are too high, and that the increase in the total solids may be accounted for on one or more of the following grounds:—1. By the greater evaporation of the milk while being weighed, owing to the large surface of the fluid exposed. 2. By the scum which inevitably forms not allowing the complete drying of the milk. 3. By a probable oxidation of the fat or other organic constituents of the milk.

It may be noticed here that while the milk solids in the asbestos are always perfectly white, those in the platinum dishes are more or less brown, clearly showing that some change takes place in the latter process which does not ensue by the asbestos method.

TABLE II.

Fat by exhaustion.	Fat by weight in flasks.	Increase in percent- age of fat by direct weighing.
3.81	3.89	0.08
4.64	4.72	0.08
5.40	5.31	—
3.90	3.88	—
3.47	3.51	0.04
3.95	3.97	0.02
6.01	6.02	0.01
4.36	4.40	0.04
3.11	3.16	0.05
3.58	3.57	—
3.81	3.84	0.03
4.38	4.47	0.09
4.31	4.34	0.03

In the first column is shown the percentage of fat obtained by exhausting the solids in asbestos by means of the Stutzer tubes; in the second are detailed those got by extracting in Soxhlet tubes and weighing the fat in flasks. Though the results obtained are very close, those obtained by direct weighing are, in almost every instance, slightly higher of the two. It will be seen, when considering the results of Table III., that the fat obtained by difference when using the Soxhlet is somewhat lower than when the Stutzer is employed, and hence the differences shown in the third column would most probably have been greater had Soxhlet tubes been used in this series. The increased percentage of fat may, therefore, be accounted for by the

* Trans. Roy. Soc. Canada, Section III., 1890.

partial oxidation of the fat when drying in the flask on the water-bath previous to weighing. The ether used was of the best German manufacture, and left no appreciable residue on evaporation.

TABLE III.

Specific gravity.	Total solids, asbestos method, average of duplicates.	Fat by Soxhlet.	Fat by Stutzer.	Increase in percentage of fat by Stutzer tube.
1032.0	12.84	3.73	3.88	0.15
1033.5	14.35	4.60	4.61	0.01
1033.0	15.21	5.33	5.56	0.23
1032.1	12.77	3.85	3.97	0.12
1032.0	11.98	3.44	3.47	0.03
1033.2	13.03	3.94	3.96	0.01
1032.1	15.31	5.95	6.05	0.10
1033.4	13.71	4.33	4.35	0.02
1032.9	12.11	3.09	3.08	—
1031.0	12.20	3.58	3.58	—
1033.2	13.16	3.79	3.82	0.03
1033.8	13.89	4.35	4.34	—
1032.6	13.50	4.26	4.31	0.05

In the asbestos method, as described by Mr. Macfarlane, Soxhlet tubes were recommended to be used for the extraction of the fat. As but two—or at most three—tubes containing the milk solids can be exhausted by this method at once, I was induced to inaugurate the experiments detailed in the above Table (III.), which shows the percentages of fat obtained by exhausting the milk solids for the same length of time (four hours) in Stutzer tubes, in which from six to eight of the glass cups can readily be treated at once, thus effecting a saving of one-third the time over the Soxhlet method. The results by both processes are very close, yet it will be noticed that in nearly every instance the Stutzer tube gives a slightly higher percentage of fat, i.e., the extraction of the fat is more

complete by the Stutzer process. This fact may be accounted for by the more frequent washing of the solids by the ether in the Stutzer tubes, as well probably as by the slightly higher temperature of the ether in these tubes. The results by the Stutzer process are therefore, I am led to believe, the nearer to the truth of the two.

Table IV. contains the results of consecutive analyses made in duplicate by the asbestos process, using the Stutzer tubes for the extraction of the fat. Where the third figure in the decimal place exceeded 5, the second decimal figure was raised.

If it be granted that the total solids and fat can be accurately determined by this method, an inspection of the above figures will clearly prove that the results are not variable, and that when duplicates are performed no large differences will have to be averaged in order to arrive at the truth. Judging from my own experience, I should say that the labour and time involved in using the asbestos method with the Stutzer tubes are about one-third less than when other processes are employed.

ADULTERATED SPIRITS OF TURPENTINE.

A CONVENIENT METHOD FOR DETECTING AND FOR ESTIMATING PETROLEUM IN SPIRITS OF TURPENTINE.

By SAMUEL J. HINSDALE, Fayetteville, N.C.

PUT ten drops of the spirits to be examined in a (moderately concave) watch-glass, and float the glass on about a quart of water which has a temperature of about 170° F. If the spirits is pure, it will evaporate and leave the glass quite dry in seven minutes. If the spirits contains even five per cent of petroleum, it will not have completely evaporated in that time.

This experiment will prove the absence or presence of petroleum in the sample.

To estimate the *percentage* of petroleum, weigh a watch-glass and put into it ten drops of the mixture, and weigh again. Put into another glass ten drops of pure spirits of turpentine, and float both glasses on about a quart of water at about 170° F.

As soon as the pure spirits has evaporated, take off the glass which contained the mixture and weigh it. The difference between this weighing and the weight of the glass will indicate the amount of petroleum in the mixture. Knowing the weight of the ten drops, the percentage can be calculated.

A bent loop of wire is convenient to place on and remove the watch-glass from the water.

The hydrometer will detect adulteration with benzene or petroleum, but it cannot be used to estimate the amount of adulteration.

The specific gravity of pure spirits of turpentine is about 0.865.

Petroleum is the usual adulterant.

TABLE IV.

Total solids.	Fat.	Solids other than fat.
13.42	4.31	9.12
13.43	4.31	
12.68	3.80	8.88
12.67	3.80	
13.13	4.35	8.78
13.12	4.35	
13.54	4.20	9.35
13.57	4.22	
17.23	8.13	9.14
17.30	8.11	
15.14	6.08	9.06
15.16	6.10	
14.09	4.61	9.49
14.07	4.58	
12.24	4.03	8.22
12.27	4.04	
12.70	3.85	8.84
12.68	3.85	

The Presence of Alcohol in Commercial Ethyl-Ether.—Th. Poleck and K. Thümmel (*Archiv. der Pharm.*).—If a clear mixture of 4.5 vols. of a saturated solution of potassium bicarbonate and 1 vol. of a saturated solution of mercuric chloride is shaken up with commercial ether, the mixture becomes turbid in ten to twenty minutes, and a white amorphous precipitate separates out. If further quantities of ether are added, all the mercury is eliminated except traces, whilst the substance which reacted upon the ether is withdrawn from the mercurial solution. The yellow or brown colour imparted to commercial ether on the addition of potassium hydroxide is occasioned by alcohol.—*Zeit. für Anal. Chemie*, Vol. xxix., Part 6.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

March 20th, 1891.

Prof. W. E. AYRTON, F.R.S., President, in the chair.

PROF. S. U. PICKERING, F.R.S., read a Paper on "*The Theory of Dissociation Into Ions and its Consequences.*"

According to this theory, electrolytes are entirely dissociated into their ions in weak solutions. This dissociation was held by Arrhenius to absorb heat, and although heat is evolved by the dissolution of hydrochloric acid, &c., it is not maintained that dissolution evolves heat, but that the heat absorbed by the decomposition of the molecule into its atoms is more than counterbalanced by the heat supposed to be evolved by the combination of the atoms with their electric charges. These actions the author considered improbable, and thought that before being accepted, the theory must give satisfactory answers to the following questions:—How can matter combine with an affection of matter to produce heat? Whence do the electric charges originate? Why does not the opposite electrification of the different atoms make them cling more firmly together, instead of dissolving the union between them; and why should an atom which possesses a strong attraction for a negative charge (such as chlorine) go to the positive electrode during electrolysis?

When a dilute solution, which is supposed to contain some gaseous molecules, is further diluted, then, according to the theory, some of the molecules are dissociated, and, if heat is absorbed, it follows that the dissociation, and therefore dissolution, of the gas must absorb heat; yet, he said, it can be shown that in some of these cases the dissolution of a gas evolves a large amount of heat.

The antagonism between the present and the old electro-chemical theory—according to which the atomic charges are identical with the free energy of an atom, and are the cause of combination, not decomposition—was commented on, as well as the disagreement between the present theory and Clausius's view that there are a few ions or atoms present in a liquid owing to accidental super-heating of some of the molecules. Reasons, however, were adduced for believing that the presence of even a few atoms in a solution to be improbable.

A communication on "*Some Points in Electrolysis*" was made by Mr. J. SWINBURNE.

Considering a reversible single fluid cell, the author, by a process of reasoning based on Carnot's principle and the conservation of energy, arrives at Helmholtz equation—

$$E = E_c + \theta \frac{dE}{d\theta}$$

where E is the electromotive force, E_c the part due to chemical action, and θ the absolute temperature. Writing the equation in full, using suffixes n and p to denote the negative and positive plates, it becomes—

$$E_n + E_p = E_{nc} + E_{pc} + \theta \frac{dE_n}{d\theta} + \theta \frac{dE_p}{d\theta}$$

He then shows that by having the two plates in different vessels and heating them to different temperatures, the Peltier effects represented by—

$$\theta \frac{dE_n}{d\theta} \quad \text{and} \quad \theta \frac{dE_p}{d\theta}$$

can be determined separately. Similarly those of a two fluid battery might be found by arranging the junction of the fluids in a third vessel.

After pointing out the desirability that the conditions under which all thermo-chemical data have been obtained should be clearly stated, he proceeded to show that any cell in which secondary actions occur (as, for example, if zinc oxide primarily formed by electrolysis were to dis-

solve in sulphuric acid), must necessarily be non reversible. He also contended that in a secondary battery the formation of lead sulphate on both plates is the essence of the cells action, and that there is no intermediate formation of PbO .

On the subject of so-called "nascent" hydrogen or oxygen, he said that reasoning from the conservation of energy showed that neither could exist. Taking the case of persulphate of iron in dilute sulphuric acid, which is said to be reduced to protosulphate by the "nascent hydrogen" liberated on putting a piece of metal (say magnesium) into the liquid, he said a better explanation of the phenomena would be that the metal dissolves if it either reduces the metal or evolves hydrogen; and as the former requires less energy, the reduction takes place, and when no reducible salt is available, hydrogen is evolved. Evolution of hydrogen, and reduction of the per salt, are thus *alternative* and not *consecutive* actions.

Examining Dr. Lodge's views on the contact E.M.F. between metals, he remarked that if the tendency of a metal (such as zinc) to oxidise can produce an electric stress or difference of potential which prevents further combination, actual combination must charge the metal, if it be insulated. A piece of sodium, however, oxidises continuously, and therefore should become charged to an enormous potential. As this effect is not known to occur, the author suggested that the Volta effect may be due to films of water, and in support of this view adduced the fact that metals, when perfectly dry, do not combine with chlorine, and that even sodium is not attacked by dry chlorine.

In the discussion on the two papers, Prof. PICKERING said the idea of nascent elements had, to a large extent, been given up by chemists, and pointed out that the fact of one reaction taking place rather than another was not merely a question of heat energy, but that a kind of chemical selection was involved.

Prof. S. P. THOMPSON recalled attention to the fact that the products of electrolysis depend on the E.M.F. employed in producing it, and thought the E.M.F. required to produce the various products might be taken as a measure of their affinities. He did not agree with Mr. Swinburne's method of finding the E.M.F. of a secondary battery from thermo-chemical data, for he failed to see how two similar actions going on at the two plates of a cell could add anything whatever to the E.M.F. of the cell.

The PRESIDENT said the question whether the potential difference between two dissimilar substances was due to oxidation or to mere contact could only be decided by direct experiments made in a vacuum, from which all traces of moisture and oxygen had been removed. Without agreeing with Dr. Lodge's view on the subject, he pointed out that the continuous oxidation of a piece of insulated sodium need not necessarily produce a great potential difference, for the combination might produce heat.

After Prof. Pickering and Mr. Swinburne had replied to the points raised, Mr. WALTER BAILEY took the chair, and

Prof. PERRY read a note "*On the Variation of Surface-Tension with Temperature,*" by Prof. A. L. SELBY, M.A.

Considering unit mass of liquid at constant volume, but variable surface (S), and temp. (t), the author expresses the gain of intrinsic energy due to changes of the variables by $dH + dW = kdt + (l + T)dS$; where dH is the heat absorbed, dW the work done on the film, k the specific heat at constant volume, l the latent heat of extension, and T the surface tension. This being a perfect differential, it is shown that $T = c - bt$, and $l = bt$, c and b being constants.

Supposing c and b to be independent of the specific volume of the liquid, it is shown that at the critical temperature $t = \frac{c}{b}$; hence, this temperature may be determined by finding the surface tension at two very different temperatures. Since, also, $l = bt$, the latent heat of extension is proportional to the absolute temperature.

Reasons for supposing *b* to be independent of the specific volume are given in the paper.

Mr. BLAKESLEY described an effect of temperature on surface tension which he had observed in sensitive spirit-levels. By warming one end of the tube, even by the hand, the bubble immediately moves towards that end. This effect, which might produce considerable error in engineering operations, was, so far as he was aware, not mentioned in the text-books.

Prof. PERRY remarked that although the volume, temperature, and surface of the liquid had been referred to in the paper, pressure was not mentioned, and on this point he enquired whether the results arrived at were true, quite independent of the pressure.

Prof. S. P. THOMPSON, D.Sc., read a paper on "*Magnetic Proof-pieces and Proof Planes.*"

The distribution of magnetism over magnets has been examined in various ways by different observers, but mostly by observing the force of detachment of either rods, ellipsoids, or spheres used as proof-pieces. In all these cases it was, the author said, difficult to see exactly what was measured; for the presence of the proof-pieces altered the thing to be tested. The pull exerted must also depend on the permeability of the piece used, as well as on its shape and disposition with respect to the magnetic circuit. He had therefore investigated the subject by finding the actual distributions by means of a flat exploring coil and ballistic galvanometer, both with and without the presence of proof-pieces of various shapes and sizes. The results show that the perturbations produced by the proof-pieces are always large, in some cases the perturbed field about a point being four to six times the unperturbed field. In most cases, however, the ratio of the perturbed to the unperturbed field was constant so long as the former did not exceed 6000 C.G.S. units.

The amount of perturbation was also found to depend on the saturation of the magnet, and on whether it was a permanent or an electro-magnet. The numbers obtained in various experiments, and curves plotted from such results, were shown.

In conclusion, the author said that in using proof-pieces much depended on the accuracy of the contact, but in any case the results obtained were not very reliable. The flat exploring coil, or magnetic proof-plane, however, furnished a satisfactory method of examining magnetic distributions.

NOTICES OF BOOKS.

The Action of Water on Lead. Being an Inquiry into the Cause and Mode of the Action and its Prevention. By J. H. GARRETT, M.D. London: H. K. Lewis.

THE presence of lead in the water supplied to many towns is certainly a serious evil, and as it has not been by all means fully understood, Dr. Garrett's contributions to the question are exceedingly valuable. It is now clear that if a water is fairly pure it is found to act upon lead or dissolve it to a certain extent, even in the absence of an acid. The author observed that distilled waters that were neutral, or even very faintly alkaline, can act upon lead. The lead, it would seem, derives the oxygen necessary for its corrosion, not so much from the free oxygen or any other oxygenous gas existing in solution in the water, as from nitrates and nitrites present. The quantity requisite for action, at least in the absence of any alkaline-earth carbonates, is extremely small. Its origin may be sought "in the decomposition of the organic matter which such waters invariably contain." Such nitrogenous matter may possibly be converted into nitric acid by the action of a bacillus. This question we agree with the author requires further study.

A careful examination was made of the water supplied to Mirfield by the Huddersfield Corporation. The author remarks that in a town in which the water, as delivered into the mains, is absolutely free from lead, it may become contaminated by means of leaden service pipes. This is especially the case where the water supply is intermittent. But even if constant, as it ought on sanitary grounds to be universally, the water from the service pipes may fall back into the mains in consequence of interchanging currents.

We may here ask whether the mechanical ingenuity of the age could not devise some arrangement which should render the reflux of water into the mains impossible. The author thinks that "in places like Mirfield no single inhabitant could protect himself by using an iron service pipe." But what if leaden service pipes were altogether prohibited.

The evidence collected from the author's experiments, which appear to have been well planned and carefully executed, leads to the conclusion that if the water contains any inorganic acid it is, in part at least, probably nitric acid.

The author's proposed remedy lies in the addition to the water of an alkaline carbonate, and especially carbonate of lime! This is not a welcome expedient. To have the skin, after washing, coated with a gluey film of lime, to find linen returned from the laundry in the same clammy condition, to partake of vegetables hardened instead of softened by boiling, are certainly a serious grievance. If the water supply is constant, and if the consumer takes the precaution of letting a few quarts of water run away from the tap every morning before any is used for drinking or cooking, the danger is reduced to the vanishing point.

Dr. Garrett's improvement on the ordinary method of testing for lead in water seems very feasible. He puts into a narrow test-tube half an ounce of the water and one drop of hydrochloric acid; passes into it washed H_2S , and adds half a grain barium sulphate. Shake, and set aside. Ammonium sulphide may be used instead of sulphuretted hydrogen, but in series of comparative experiments one and the same precipitant should always be used.

Dr. Garrett may be congratulated on the thoroughness and the value of his researches.

Kelly's London Medical Directory, 1891. London Kelly and Co.

WE have here a work filling a vacancy which had become more and more widely felt. The compilers give the names, addresses, qualifications, and works, if any, of all qualified medical men in practice in the Metropolitan district. In addition it furnishes particulars concerning hospitals, public analysts, learned societies, medical and scientific publications, insurance companies, lunatic asylums, and examining bodies.

Turning firstly to the section on scientific societies, we note a few defects which will doubtless not reappear in next year's issue. Thus there is no mention of the Society for the Promotion of Medicine by Research, which we hope is not defunct, the South London Microscopical Society, and the South London Entomological and Natural History Society—a very numerous body. The anti-scientific societies are deservedly ignored.

Turning to the medical and scientific publications we find the names of two "weeklies" which, to our great regret, have ceased to appear.

A glance at the main body of this directory, the muster roll of practitioners will prove that the labour incurred in its compilation must have been very heavy, and we cannot feel surprised if a few mistakes have occurred. We wish the publishers the success which they have so fully merited.

Notes of a Thousand Men and Some Things they did in Art, Literature, War, Government, Science, and Industry. Arranged in Group and in Order of Time. By DAVID K. MORRIS. London: Cassell and Co. (for the Author).

THE idea of this work is novel, and it will, in our opinion, often prove useful. It gives in parallel columns the names of the eminent characters, the date and place of their birth, the date and place of their death, and their works, discoveries, inventions, or achievements. As a rule, living celebrities are prudently omitted. As regards the selection of the "thousand men," no objection can fairly be raised. The weak point of the work lies in its classifications. It is strange to find Gilbert White placed, not among zoologists, but among the essayists and critics. Ure, in virtue of his *Dictionaries of Chemistry and of Arts and Manufactures*, is made to figure among lexicographers, whilst H. Watts and A. Würtz, also the authors of *Dictionaries of Chemistry*, rightly rank among chemists. Perhaps the only statement which we can formally question, often as it has been repeated, is that the works of Celsus were burnt by the Caliph Omar in A.D. 640. The balance of evidence now seems to show that the Alexandrian Library was destroyed by the Bishop Cyril and his monks at an earlier date.

A reflection which must strike the reader is that scientific men and brain-workers generally are long-lived.

A Treatise on the Law and Practice relating to Letters Patent for Inventions, with an Appendix of Statutes, International Convention, Rules, Forms and Precedents, Orders, &c. By ROBERT FROST, B.Sc., F.C.S., Barrister-at-Law. London: Stevens and Haynes.

THERE are obviously two points of view from which a treatise on patent-law might be written. On the one hand, it would be possible to show what a patent-law ought to be to answer its purpose, that is to confer the maximum possible advantage on the arts, manufactures, and commerce of the nation, to examine in what respects our present system falls short of this ideal, and how it might best be amended. On the other hand, such a treatise like the work before us might simply expound the law as it stands, carefully keeping back any aspirations after its higher development. We must not imagine that the compilation of such a treatise is an easy task. In a country where the patent-law is not codified, and where its decision on any contested point can be gathered merely by the tedious and often difficult task of collating statutes and judicial decisions, how differently the statutes and precedents may be interpreted by different judges it is not necessary to show.

At the same time we must remember that tedious and costly litigation concerning patents cannot be excluded either by a codified patent-law or by a rigid preliminary examination. In proof of this we need only refer to the patent-suits in Germany, in France, and in the United States.

The author, in discussing the subject-matter of letters patent, lays down, very rationally, the principle that "an art which is to be exercised for the sole object of breaking the law, or for the sole object of producing anything designed to be used for any illegal purpose, cannot form the subject-matter of valid letters-patent." It is to be feared, however, that a patent has been granted for a fraud, in the shape of moulding worthless pastes or powders into the form of coffee-berries, or by analogy of other seeds, fruits, or berries.

We are happy to learn that "patents will not in future be granted to agents resident abroad in respect of inventions communicated to them by aliens also resident abroad."

As regards "communications from abroad" it seems very clear that patents were originally granted for such com-

munications in order that some new art or manufacture may be introduced into the realm. At present such communications are made to have the very opposite effect, viz., of keeping new arts out. An alien communicates his invention to some agent, who then obtains a patent for it in his own name, but immediately conveys it exclusively to the alien, whose sole object in the transaction is to *prevent* the art from being worked in Britain.

It has been held, we are told, that "the prior user of an invention in a colony forms no legal bar to the granting of a patent for the same invention in this country." This is gravely to be regretted, since the principle thus involved will form a bar to the adoption of an imperial patent-law.

The question of utility is discussed at some length. Utility in law is not utility in the common sense of the term, but merely means "an invention better than the preceding knowledge of the trade as to a particular fabric." This is the more important because not a few very successful inventions, very lucrative to the patentee, are completely devoid of utility in the ordinary acceptation.

Without further extending our examination of this work, it has been the outcome of careful and prolonged study, and it cannot fail to prove extremely valuable to patent-agents as well as to counsel and solicitors engaged in patent-cases.

The Electro-Platers' Handbook: A Practical Manual for Amateurs and Young Students in Electro-Metallurgy. By G. E. BONNEY. With 61 Illustrations. London: Whittaker and Co., 1891.

LIKE other departments of industrial art, electro-metallurgy is receiving an increased share of attention. Mr. Bonney undertakes in the present work to guide the amateur experimentalist through a field which is by no means free from difficulties. In this task he is very fairly successful.

After some preliminary matter, he classifies the metals as those of low and high cost, and again as those easily and not easily deposited. He gives a notice of the batteries most suitable for electro-deposition, and gives instructions on their management. Then follow dynamos of various kinds. The one which will ultimately survive is, he considers, a "long drum running in a single magnet type of field, which for plating must be shunt-wound." An instrument for indicating the speed of a dynamo, here described and figured, bears the barbarous name of the speedometer.

In a section on thermometers and hydrometers, the author performs the novel feat of giving a formula for recalculating degrees Baumé into degrees direct specific gravity. But as the Baumé instruments do not agree among themselves, the rule will not always work smoothly. For the respective conversion of degrees Twaddell and direct specific gravity, he gives no formula, as any reader can deduce it from an inspection of the two scales.

The remarks on cleanliness are by no means needless; it is not easy to convince the student and the amateur to what a degree the cleanliness demanded in the laboratory transcends that of the best-managed household.

To nickel he scarcely does justice. If pure, i.e., free from copper, arsenic, &c., its salts are scarcely more poisonous than those of iron.

The table of combining weights at the end of the book—Mr. Bonney does not say atomic weights, though the figures given are clearly meant for the latter—is not on a level with the most recent determinations. The atomic weights of platinum and indium are made equal, and both are higher than that of gold—an inveterate error which we hope to see corrected in the next edition. The work is of evident utility, and has before it a future.

CORRESPONDENCE.

PALMELLINE AND ASPERGILLINE.

To the Editor of the Chemical News.

SIR,—It appears from your paragraph (CHEM. NEWS, vol. lxi., p. 153) that the "vegetable hematine"—the pigment of the spores of *Aspergillus niger*—from its striking analogies with the hematine of the blood, must be identical with the substance palmelline extracted by me from *Palmella cruenta* in 1879, accounts of which were published in the CHEMICAL NEWS and in the *Comptes Rendus* for that year. I proved the absorption-spectrum of palmelline to be very similar, if not identical, to that of the blood. It is singular that old botanists should have named the alga in question *Chaos sanguinea*, and the moderns *Palmella "cruenta"*, since the resemblance with blood goes beyond the mere external appearance.—I am, &c.,

T. L. PHIPSON.

Putney, March 27, 1891.

SEWAGE PURIFICATION.

To the Editor of the Chemical News.

SIR,—My attention has been called to the last issue of your esteemed journal, in which you reply to your correspondent, W. Naylor, "We know of no method of sterilising sewage."

I take the liberty of handing you herewith our pamphlet containing copies of reports by Dr. E. Klein, F.R.S., the eminent bacteriologist, and by Mr. Cassal, F.I.C., Public Analyst, on the results of their independent and exhaustive investigations of the effect of the "Amines" process as applied to the treatment of sewage. Since both certify to the absolute sterility of the effluent, I should deem it a favour if, after perusal of the said reports, you can see your way to giving publicity in your next issue to the facts above stated, so that your correspondent may obtain correct information upon the point.—I am, &c.,

HUGO WOLLHEIM, Managing Director.

The "Amines" Syndicate, Limited,
101, Leadenhall St., E.C.
London, April 1, 1891.

Determination of Dry Matter in Fibrous Materials.

—O. Knöfler (*Papier Zeitung*).—The apparatus consists of a cylindrical water-bath in which is introduced the recipient for the samples, consisting of two concentric cylinders with bottoms. In this is suspended a wire basket containing the sample fixed to one arm of a balance. The other arm is like Westphal's balance, provided with a counterpoise to the wire basket, and graduated in 10 parts. So much of the sample is used as the large rider weighs, so that the balance is in equilibrium when it is placed at the mark 10. When the desiccation has gone on for a time the balance is again brought to an equilibrium by displacing the large rider, and putting on the smaller 10 and 100 riders, and observing if the weight is constant. The percentage of dry matter is then read off from the position of the riders.

Determination of Paraffin, Ceresine, and Mineral Oils in Fats and Waxes.—F. M. Horn (*Zeit. Angew. Chemie*).—The sample is generally saponified, and the soap is extracted with petroleum ether. This method is not quite trustworthy in presence of mineral oils, as in this case a part of the soap dissolves in petroleum ether. The author therefore prefers to extract the dried soap with boiling chloroform in Soxhlet's apparatus.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxii., No. 10, March 9, 1891.

On the Hydrated Sodium Manganates.—G. Rousseau.—If sodium manganate is heated from 300° to white redness it undergoes a series of curious metamorphoses. There is first formed the hydrate (old notation), $8\text{MnO}_2\text{NaO}_5\text{HO}$. From about 500° this product tends to become polymerised, and at 800° it changes into the hydrate, $12\text{MnO}_2\text{NaO}_4\text{HO}$. About 1000° there appears a more complex compound, $16\text{MnO}_2\text{NaO}_8\text{HO}$; then between 1200° and 1300° we return to the manganite, $8\text{MnO}_2\text{NaO}_5\text{HO}$, which was originally formed at 300°. Finally at white redness the hydrate, $12\text{MnO}_2\text{NaO}_4\text{HO}$ reappears, as if a new cycle parallel to the former was about to be produced. The author has already pointed out analogous variations in the condensation of the alkaline earthy manganites, but these compounds were anhydrous. On the other hand, the hydrated alkaline ferrites and platinates which he has discovered do not form cycles in their successive changes. The union of these two orders of phenomena in one and the same group of compounds constitutes a novel fact to which he wishes to call the attention of chemists.

On the Transformation of Sodium Pyrophosphate into an Acid Phosphite.—L. Amat.—The object of the present memoir is to trace the laws of this transformation, noting especially the influence of time and that of dilution.

On Silicibromoform.—A. Besson.—This compound is a colourless liquid which in an inert gas distils over without decomposition at 109°–111°, and does not solidify at 60°. It gives off copious fumes, and finally ignites spontaneously in contact with air. The vapour forms detonating mixtures with air. It is decomposed with violence by water and alkalis. Ammoniacal gas reacts upon silicibromoform, and if the reaction is not moderated there is a development not merely of heat but of light.

Thermic Study of Certain Alkaline Derivatives of Erythrit.—M. de Forcrand.—A thermo-chemical paper, the main portion of which does not admit of useful reproduction. The formation heats of the sodium alcoholates increase regularly with the degree of atomicity. For the potassium derivatives the corresponding numbers are higher and increase in the same manner.

On Some Ammoniacal Compounds of Mercury Cyanide.—Raoul Varet.—The compounds studied are the mercury-copper bromo-cyanide, the mercury-cadmium bromo-cyanides, the mercury-cadmium iodo-cyanide, the corresponding chloro-cyanide and the mercury-nickel chlorocyanide.

Fermentation of Starch by the Action of the Butyric Ferment.—A. Villiers.—The author has previously shown that if potato-starch is allowed to ferment under the action of *Bacillus amylobacter* the products are chiefly dextrines. At the same time there are formed certain carbohydrates which the author names celluloses, and to which he assigns the composition $\text{C}_{12}\text{H}_{10}\text{O}_{10} + 3\text{HO}$ and $(\text{C}_{12}\text{H}_{10}\text{O}_{10}) \cdot \text{C}_4\text{H}_6\text{O}_2 + 10\text{HO}$. These compounds differ very decidedly from the saccharines. The latter especially does not melt at temperatures within the thermometric scale. It is not fermentible, and does not reduce the cupro-potassic solution.

Vol. cxii., No. 11, March 16, 1891.

On the Different Manifestations of the Phosphorescence of Minerals under the Influence of Light or of Heat.—H. Becquerel.—In the phosphoro-

scope we recognise that one and the same body may emit several different spectra; these spectra are distinguished from each other by the duration of the luminous emission. The researches which the author published some years ago on the variation of the absorption spectra and on their relations with the spectra of phosphorescence justify the conclusion that the various spectra of one and the same body are due to the presence in this body of different substances or of different compounds of the same substance. The light of the electric spark striking near bodies induces phosphorescence like the solar light, and the emission spectra are the same. Heat, in the luminous form, restores to bodies a limited quantity of energy. When this quantity is exhausted, the bodies no longer phosphoresce by heat. If the necessary energy is restored to them by the action of an electric spark or by exposure to light, they phosphoresce again when heated. The brilliant bands of the spectra emitted under the influence of heat are the same as those in the phosphorescence, but they have different relative intensities.

The Transformations which Accompany the Carburation of Iron by the Diamond.—F. Osmond.—The author's results show that diamond in itself does not cement iron, but first undergoes in contact with the metal a molecular transformation which makes it capable of cementation. The diffusion of carbon in the iron involves as a corollary a diffusion of iron in the transformed diamond.

The Formation of Coloured Lakes.—Lés Vignon.—The absorption of a basic colouring matter coincides with the existence of intense acid fundions in the absorbing substance; if these decrease, the absorbent power is enfeebled and disappears.

Researches on Dispersion in Organic Compounds (Ethers).—Ph. Barbier and L. Roux.—In the series of ethers examined the specific dispersion powers increase progressively with the molecular condensation. The mean of the differences between two consecutive values of the molecular dispersive powers is approximately constant and equal to 7.5.

Influence of Extractive Matters on the Real Alcoholic Standard of Spirits.—Ch. Blarez.—This paper requires the accompanying tables.

MISCELLANEOUS.

Royal Institution.—Mr. J. Scott Keltie will, on Tuesday, April 7th, begin a course of three lectures on "The Geography of Africa, with special reference to the Exploration, Commercial Development, and Political Partition of the Continent." Professor Dewar will, on Thursday, April 9th, begin a course of six lectures on "Recent Spectroscopic Investigations," and Professor Silvanus P. Thompson will, on Saturday, April 11th, begin a course of four lectures on "The Dynamo." The Friday Evening Meetings will be resumed on April 10th, when Sir William Thomson will give a discourse on "Electric and Magnetic Screening."

Camera Club.—The 1891 Conference will be held in the Theatre of the Society of Arts on Tuesday and Wednesday, April 7th and 8th, under the presidency of Captain W. de W. Abney, C.B., D.C.L., R.E., F.R.S. Tuesday, April 7th, papers will be read from 2 p.m. to 5.30 p.m., in the Theatre: Captain W. de W. Abney, R.E., C.B., D.C.L., F.R.S., Presidential address; Mr. Lionel Clark, C.E., "The Use of Uncorrected Lenses"; Mr. Joseph Pennell, "Photography as a Hindrance and a Help to Art"; Rev. F. C. Lambert, M.A., "Note on the Physiological Aspect of Some Problems in Art." At 8 p.m., exhibition of lantern slides in the Theatre. Wednesday, April 8th, 2 p.m., papers to be read from 2 p.m. to 5.30 p.m.: Major J. F. Nott, "Photography

and Illustrated Journalism"; Mr. C. V. Boys, "An Application of Photography"; Sir H. T. Wood, subject will be announced later. 7.30 p.m., Annual Club Dinner for Members and friends at the Criterion Restaurant. The Annual Exhibition of Photographs by Members will be on view in the Club House Meeting Room, Charing Cross Road, from 10 a.m. to 4 p.m. Admission by card from any member of the club, or by ticket from the hon. sec. The exhibition will be open under these conditions for about six weeks from Tuesday, April 7th.

MEETINGS FOR THE WEEK.

- MONDAY, 6th.**—Medical, 8.30.
— Royal Institution, 5. General Monthly Meeting.
— Society of Chemical Industry, 8. (1) "The Analysis of Illuminating Gases." (2) "The Products of Checked Combustion," by Professor Vivian B. Lewes.
- TUESDAY, 7th.**—Institute of Civil Engineers, 8.
— Pathological, 8.30
— Royal Institution, 3. "The Geography of Africa," by J. Scott Keltie, F.R.G.S.
- WEDNESDAY, 8th.**—Geological, 8.
— Pharmaceutical, 8.
— Society of Arts, 8. "The Durability of Pictures Painted with Oils and Varnishes," by A. P. Laurie.
- THURSDAY, 9th.**—Royal, 4.30.
— Mathematical, 8.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "Recent Spectroscopic Investigations," by Prof. Dewar, M.A., F.R.S.
— Society of Arts, 8. "The Indian Village Community," with special reference to Modern Investigation," by B. H. Baden-Powell, C.I.E., late Bengal C.S. (Purjab).
- FRIDAY, 10th.**—Astronomical, 8.
— Royal Institution, 9. "Electric and Magnetic Screening," by Sir William Thomson, D.C.L., LL.D., Pres. R.S.
- SATURDAY, 11th.**—Royal Institution, 3. "The Dynamo," by Prof. Silvanus P. Thompson, D.Sc., B.A.

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ST. PAUL'S SCHOOL.—An Examination for filling up Three Vacancies on the Foundation will be held on the 8th April next.—For information apply to the Bursar, St. Paul's School, West Kensington.

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THE CHEMICAL NEWS.

Vol. LXIII., No. 1637.

VAN 'T HOFF'S LAW OF OSMOTIC PRESSURE.

By D. J. CARNEGIE.

THERE are few, I think, who would oppose the application of the qualification "epoch-making" to the recent work of Van 't Hoff in connection with the osmotic pressures of dilute solutions.

Although this work involves nothing of what is popularly styled scientific romance, and is of too specialised a nature to beget the general interest of the public, yet it must be admitted that, taken along with its immediate consequences, it appeared at first sight very much in the light of romance to the smaller world of scientists, whose thoughts and energies it has, notwithstanding, rolled into altogether new courses.

Before detailing this work, however, certain preliminaries are necessary to the full appreciation of the position it assumes in the province of knowledge to which it essentially belongs.

Matter exists in three states: solid, liquid, and gaseous. Up till quite recent times theoretical chemistry has had chiefly to do with matter in its gaseous condition. The deportment of gaseous matter is conditioned by very simple laws, the chief of these being (1) Boyle's law, (2) Charles's law (Gay Lussac's law), (3) Avogadro's law, and (4) Graham's law.

In his "defence of the doctrine touching the weight and spring of the air" (1662), Boyle very quaintly describes how, by means of "a tube crooked at the bottom through the instrumentality of a dextrous hand and a lamp," he discovered "not without delight and satisfaction," that the volume of a constant mass of gas varies inversely as the applied pressure; or expressed algebraically, $p \propto 1/v$.

Then in 1787 followed Charles's law, which ultimately giving rise to the conception of an absolute zero of temperature finds its fullest enunciation in the form; the volume of a constant mass of gas at constant pressure is proportional to its absolute temperature, or $v \propto t$.

In 1811 Avogadro laid the foundation of modern chemistry in advancing the hypothesis that equal volumes of gases under like conditions of temperature and pressure contain equal numbers of molecules. Expressed algebraically, molecular weight = $2 \times$ specific gravity of gas. This hypothesis (raised to the rank of a law by the Kinetic theory of gases) lies at the foundation of all the fundamental constants of chemistry—the atomic weights; and till within quite recent times has been the only method of any generality for determining molecular weights, and through these atomic weights.

Graham (1833), following up some of Döbereiner's experiments, which had their origin in a small crack in a glass gas receiver, discovered empirically that the rates of diffusion of gases through very small openings are inversely proportional to the square roots of their specific gravities; or—

$$\frac{\text{Rate of diffusion of } x}{\text{Rate of diffusion of } y} = \frac{\sqrt{\text{Specific gravity } y}}{\sqrt{\text{Specific gravity } x}}$$

Before inquiring what laws, having a chemical bearing, pertain to matter in the liquid state, it will be well to divide liquids into the sub-classes homogeneous liquids (such as mercury, molten sulphur), and non-homogeneous liquids or solutions (such as solution of sugar in water). It is the latter sub-division with which we have to do.

In 1867, Guldberg and Waage, in enunciating their law to the effect that chemical action which takes place between substances in solution is proportional to the active masses of each of the substances participating in the reaction, laid the foundation of modern concepts regarding chemical affinity.

Quite recently, Raoult in showing that equimolecular solutions (i.e., solutions consisting of quantities of substances proportional to their molecular weights, dissolved in equal quantities of solvent), have the same freezing points and vapour tensions, furnished two new methods of wide applicability for determining molecular weights—methods which can be applied where Avogadro's law fails. Expressed algebraically, Raoult's laws stand as follows:—

$$m = \frac{p M f^1}{(f - f^1) P} \quad m = \frac{r p}{\Delta P}$$

The molecular theory of matter has found its greatest development in its application to matter in the gaseous state, that is, as the Kinetic theory of gases. Allow that heat is essentially a molecular movement, and that the pressure of a gas is due not to any specific repulsive forces indwelling in the molecules, but merely to the repeated impacts on the sides of the containing vessel of the heat-impelled molecules, then the laws of Boyle, Charles, Avogadro, and Graham, following as necessary consequences of these postulates, are raised from the low level of mere empiricisms to the higher platform of logical deductions from a theory which, involving only the most simple and probable premises, co-ordinates and explains a vast number of at first apparently disconnected facts.

The question now arises, are our theories respecting the structure and mechanism of liquids (the case of solids does not concern us in this paper), as definite as the Kinetic theory of gases, so that they, in an analogous way, confer warranty on the laws conditioning the properties of liquids? In answer we must reply that up to the present time our views regarding the constitution of homogeneous liquids are so vague as to scarcely merit the name of theories, and that the nature of non-homogeneous liquids or solutions is a burning question of today's theoretical chemistry, which is dividing chemist against chemist.

By no means the least result of Van't Hoff's work on osmotic pressure is the elucidation of the nature, if not of solutions generally, at least of that important class of solutions—the dilute solutions which Raoult and others have experimentally investigated. What is this quantity—osmotic pressure? Suppose a vessel A, filled with, say, sugar solution, and immersed completely in water as in Fig. 1. Further, suppose the walls of A of such a nature that they permit the passage through them of water, but not of sugar molecules. Such walls Van't Hoff calls *semi-permeable*. In virtue of the attraction of sugar molecules for water molecules, water will enter the vessel A, thereby increasing the pressure on its sides up to a certain limit when equilibrium is established. This equilibrium pressure in A is called osmotic pressure.

Such *semi-permeable* vessels are realised in practice as follows. The porous cell A, Fig. 2, filled with a solution of potassium ferrocyanide, is immersed in a beaker containing a solution of copper sulphate. The solutions diffusing into the walls of the cell, and meeting about half way, react, forming a precipitate, s, of insoluble copper ferrocyanide, which possesses the semi-permeable qualities alluded to.

In order to take a measure of osmotic pressure with the cell, it is washed out, filled with a solution of known strength of the substance to be investigated, and closed air-tight by cementing in the glass head piece, H, which

* Where m = molecular weight to be ascertained, M = molecular weight of solvent, P = weight of solvent, p = weight of dissolved body, f^1 = vapour pressure of solution, f = ditto for solvent, Δ = lowering of freezing-point produced by dissolving p grms. of substance in P grms. of solution, and r = constant depending on solvent and determined experimentally for each solvent.

carries the manometer, M. The whole apparatus immersed in a beaker of pure water is allowed to stand till the mercury levels in the manometer cease to change. The difference in height in the levels in the two limbs gives the osmotic pressure.

Accepting this definition of osmotic pressure, Van't Hoff asserts the existence of a very close and deep seated analogy between gases and substances in dilute solution, provided always in dealing with the analogy we make osmotic pressure in solutions as thus determined correspond to gaseous pressure.

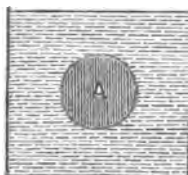


FIG. 1.

Now Boyle's law states that pressure varies inversely as volume, or what is the same thing, varies directly as concentration. If Van't Hoff's asserted analogy be valid the osmotic pressure of a solution should vary directly as its concentration. The following measurements made by Pfeffer shows that Boyle's law *does* hold for dilute solutions, provided osmotic pressure be substituted for gaseous pressure in the enunciation of the law.

Concentration in percentages.	Osmotic pressure in m.m. of mercury.	Ratio : Pressure to Concentration.
1	535	535
2	1016	508
2.74	1518	554
4	2082	521
6	3075	513

It will be noticed that the figures in the third column in conformity with Boyle's law are approximately constant. That Charles's law also holds for dilute solutions

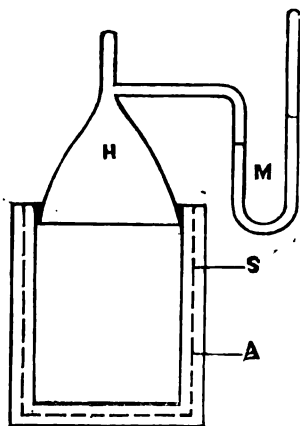


FIG. 2.

has been proved in several ways. I select as the most interesting a physiological method of proof which we owe to De Vries. A leaf—all of such a plant as *Tradescantia discolor* (one of the plants actually used)—consists essentially of an outer cell wall, C, Fig. 3, lined by a layer of protoplasm, the primordial utricle P; the double envelope forming the boundary of the vacuole V, which is filled with cell sap.

The living primordial utricle has all the properties of a semi-permeable membrane; consequently, if the cell be

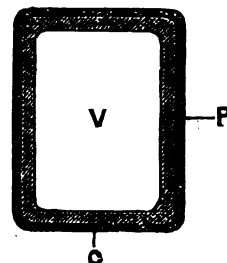


FIG. 3.

immersed in a solution having a greater osmotic pressure than that of the cell sap (due to its contained organic acids and acid salts), water will pass from the sap to the surrounding solution, and the cell will assume a *plasmolytic* condition. That is, the primordial utricle will leave the cell wall, and contract on its diminished sap contents, as represented in Fig. 4.

If the concentration of the surrounding solution be so arranged that its osmotic pressure is equal to that of the

sap, then there will be no plasmolysis—the primordial utricle will remain in close contact with the cell wall. Of course, if two different solutions are in osmotic equilibrium with the same cell, they must be in osmotic equilibrium with each other. Taking advantage of this behaviour of vegetable cells, it has been shown that solutions of common salt, nitre, and sugar, which exert equal osmotic pressure (*i.e.*, are *isotonic*) at 0°, are isotonic also at 34°. But this is none other than an indirect admission that Charles's law holds also for dilute solutions.

So far as I am aware, dilute solutions have not yet been investigated with respect to Graham's law. With the aid of a cylinder with semi-permeable walls fitted with a piston, we can conceive of various *reversible* processes to which these dilute solutions may be submitted. But that protean and powerful law—the second law of thermodynamics (which states that the energy at our disposal, though unchangeable in amount, is continually approaching a dead level condition in which it will no longer be available), deals with *reversible cycles*, and Van't Hoff has shown that by applying this second law of thermodynamics to a special reversible process carried

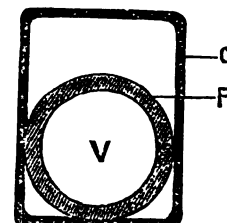


FIG. 4.

out without change of temperature, the necessary consequence is that the osmotic pressure exerted by a dilute solution of a substance is equal to the gaseous pressure which the substance would exert under the same conditions of temperature and concentration. Hence, suppose we have x grms. of a substance dissolved in V volumes of a solvent exerting an osmotic pressure P at t° ; then x grms. of the same substance in the gaseous state, occupying V volumes at t° would exert a gaseous pressure $= P$.

It is but a short step further to conclude that Avogadro's law holds also for dilute solutions, and that under equal osmotic pressures, and at the same temperature, equal volumes of dilute solutions contain equal numbers of dissolved molecules; and, moreover, the same numbers

of molecules which would be contained in equal volumes of gases under like conditions of temperature and pressure. This is Van 't Hoff's law of osmotic pressure, which has been amply confirmed by experiment.

But further, assuming the truth of all that has preceded, and applying the second law of thermodynamics to other reversible processes suitably conceived,* and carried out with the cylinder of semi-permeable material; and Van 't Hoff shows that the important laws of Raoult in all their entirety are direct consequences of this analogy between gases and dilute solutions. Nay more, the equations arrived at have new information of their own, and show that the constant ν in Raoult's second equation (see *ante*), which up to date has only been determinable by experiment, may be easily calculated from a knowledge of the freezing-point and heat of fusion of the solvent; the calculated results agreeing very closely with the experimentally observed results.

By similar methods of reasoning, he has lastly shown that Guldberg and Waage's law (in a slightly modified and more exact form), is a necessary consequence of his development of the conception of osmotic pressure.

Thus we see that the laws relating to dilute solutions, Boyle's law, Charles's law, Raoult's law, Avogadro's law, and Guldberg's law, are not disconnected and independent truths; just as the kinetic theory of gases co-ordinated the laws regulating the deportment of gases, and gave them an imprimatur which they did not before possess, so the analogy worked out by Van 't Hoff has resulted, not only in the discovery of new and unsuspected laws for non-homogeneous liquids, but also in the power to group together new and old, and to regard, from a common standpoint, laws, which having a wide applicability, we are glad to have established and confirmed by theoretical deductions.

No longer do we, in a vague blotting-paper impression way, picture to ourselves a dilute aqueous solution of a substance as consisting of various ill-defined hydrates of the dissolved body diffused through the inert excess of solvent; on the contrary, the molecules of the dissolved body retain their individuality just as they would were the body gasified instead of dissolved, with this difference, however, that in the former case the molecules would be separated from one another by the inert ether of space, while in the latter case the molecules are kept outside each other's spheres of action by the intercalated molecules of solvent which are not always inert, but demand the introduction of constants peculiar to the solvents employed into certain of the equations conditioning the properties of solutions.

In conclusion, let us glance at the fringe of the vast sheet of consequences of Van 't Hoff's analogy. Notable exceptions to Avogadro's law occur among gases. Thus the gas of ammonium chloride under certain conditions exerts a pressure double that which Avogadro's law would lead us to expect under the conditions. Such cases are, as is well known, explained satisfactorily in terms of the theory of dissociation. The question naturally arises: Is the analogy between gases and dilute solutions so perfect that the latter also afford examples of deviation from Avogadro's law, explicable in terms of dissociation?

The answer is an affirmative.

A dilute solution of potassium chloride exerts twice the osmotic pressure that theory demands; it is hence concluded that in dilute solution each molecule of KCl is dissociated into its ions K and Cl. So startling is this and similar conclusions, that had they not been backed up by scientists of such authority as Ostwald, van 't Hoff, and Arrhenius, I doubt whether they would have ever been granted a fair hearing.

But it must not be supposed that such conclusions rest merely on analogy. Ostwald has described a simple experiment which points to the existence of free ions in a dilute solution of potassium chloride.

Further, it has been noted that those substances which in solution do not conform to van 't Hoff's law are all electrolytes, while all non-electrolytes obey the law of osmotic pressures. Now, Clausius and Williamson, years ago, suggested that the explanation of electrolysis was to be found in a partial dissociation into their ions of those substances which are electrolysable. Modern research in defining and confirming their views has shown that the very partial dissociation which these scientists were thought bold for asserting is in reality anything else but partial. In fact, in the case of those substances which we have been in the habit of regarding as most stable (HCl, KCl, KOH, &c.), the dissociation in solution is almost, if not quite, perfect; water completely, or nearly so, separating the molecule of the dissolved substance into its ions. So intimate, indeed, is the relation between electrolysis and osmotic pressure, that the latter quantity for any substance may be fully determined from measurements of the electric conductivity of its aqueous solutions.

Accepting this view of the general existence of dissociation in solution, which has arisen out of van 't Hoff's law of osmotic pressure, many purely chemical facts, hitherto inexplicable, receive a *rationale*. We can now account for Hess's law of thermo-neutrality, which states that the mixture of two neutral salt solutions is unattended by any thermal disturbance; we can now understand why the heats of neutralisation of all strong acids is approximately constant; we can conceive of a strong acid displacing a weaker acid from combination without introducing vague views on chemical forces and chimerical attractions; we begin to see through such everyday and familiar experiences as the fact that solution of silver nitrate does not produce a precipitate of silver chloride in all solutions of chlorinated compounds; in short, the development of van 't Hoff's views leads us to look on many otherwise inexplicable and seemingly isolated phenomena as part and parcel of one vast harmonious system.

"Where order in variety we see,
And where, though all things differ, all agree."

Colorado College, Colorado Springs, U.S.A.

DISCUSSION ON THE THEORY OF SOLUTION.*

(Concluded from p. 159).

PROFESSOR VAN 'T HOFF stated his conviction that we were forced on theoretical grounds, thermodynamic as well as kinetic, to admit in dilute solutions a law corresponding to that of Avogadro, differing from this only in its bearing upon "osmotic" instead of "ordinary" pressure. He insisted on the necessity of dissociation in the case of KCl as a consequence which, on this line of argument, it was impossible to escape from. On the other hand, an ordinary separation into free atoms was in evident contradiction to all we knew about them, as in the vapour of iodine and mercury. These objections become invalid when we admit a splitting up into ions, which by their enormous electrical charge ought to be widely different from what we might expect in ordinary atoms, and hence it is that Arrhenius's "electrolytic dissociation hypothesis" was at once most favourably received by the adherents of the "osmotic pressure theory." Since then both have become closely allied by the fact that the dissociated fraction, according to the last, agreed with that admitted by the first on wholly different grounds.

In reply to the objections raised by Professor Fitzgerald, it may be observed, with respect to the theoretical foundation of the osmotic pressure law, that the action on

* For details see Translation of Van 't Hoff's paper in *Phil. Mag.*, August, 1888.

* British Association (Section B), Leeds Meeting, 1890.

a semipermeable diaphragm is due, partly to the shock of the dissolved molecules, partly to the difference of forces acting upon them, from the solvent on one side, and from the solution on the other. Now, the result of the shock is directly proportional to the concentration, whereas that of the attraction is proportional to the square: thus in very dilute solutions the second action vanishes when compared with the first, and the shock is alone the origin of pressure as it is in gases. However, he insisted on these views as more intended to popularise than to prove the laws in question. If we want to do the last on kinetic grounds, we must take everything into account—movement of the molecules of the two substances mixed, action on themselves and on each other. Now, this has been just recently done by van der Waals, and the result is a very complicated formula, simplified, however, for dilute solutions into this statement, "that the dissolved molecules act on a semi-permeable membrane with strictly the same force as they would do on an ordinary membrane in the gaseous state." So from a kinetic point of view the law of Avogadro and the "osmotic pressure" law stand on the same basis.

Mr. Pickering commits a fundamental error in supposing that the osmotic pressure theory arrives at 0.63 as the number with which we had to multiply the solvent's molecular weight in order to get the so-called "constant of depression." Such conclusion was never drawn from

the theory in question; it was the formula $\frac{0.02T^2}{W}$ that

was deduced. The value 0.63 was an empirical one, introduced by Raoult. This difference has urged Professor Eykman to a very extensive experimental research, the conclusion of which was so evident that in the July number of the *Annales de Chimie et de Physique* Raoult

openly accepts the value $\frac{0.02T^2}{W}$. On p. 359 Raoult

states:—"L'abaissement α du point de congélation produit par une molécule dissoute dans 100 molécules dissolvantes est, d'après M. van 't Hoff, donné par l'expression

$\alpha = 0.02 \frac{T^2}{L}$, dans laquelle T est la température abso-

lue de congélation et L sa chaleur latente moléculaire de fusion." In addition, on p. 361, he says:—"L'accord entre l'expérience et la théorie est donc, sur tous les points, aussi complet qu'on peut le désirer en pareille matière." No one now defends the value 0.63, and a good deal of the objection which Mr. Pickering directs against it has no bearing on the osmotic pressure theory itself.

Mr. W. N. SHAW remarked that the meaning of the term solvent used by physicists when referring to water, alcohol, and the like, is somewhat widely extended when it is understood to include $100\text{H}_2\text{SO}_4$, H_2O , and the other equally complex solvents of Table I. of Mr. Pickering's paper.

An ordinary solvent could not fairly be regarded as being "inert" and "having no action whatever" when it was claimed that the solvent caused the dissociation of a large portion of the dissolved salt. The action is in fact most remarkable, and is the important point now requiring investigation and explanation. This action has been clearly illustrated by Mr. W. C. C. (Phil. Mag., May, 1890, p. 383), who has endeavoured at Cambridge to ascertain the circumstances under which stannic chloride can be brought into the dissociated or electrolytic condition. The compound is interesting, since water and alcohol produce well-known and remarkable actions upon it; moreover it is comparatively easily prepared in the pure state. It appears from the paper referred to that stannic chloride can be mixed with chloroform without receiving any conducting power. It will also absorb a considerable quantity of dry H_2S gas without chemical action, and again without becoming electrolytic; whereas the addition of a drop of water or alcohol to the non-

electrolytic mixture immediately gives rise to chemical action with a deposit of tin sulphide, the liquid becoming at the same time electrolytic.

The action of water or alcohol seems to be clearly different in this case in some fundamental manner from that of H_2S or chloroform.

Mr. Shaw also drew attention to the diagram (fig. 1) in Mr. Pickering's paper, from which, if he understood it correctly, it appears that for very weak solutions the "molecular depressions" produced by certain salts are the same for solutions containing 0.08 molecule per $100\text{H}_2\text{O}$ as they are for infinitely dilute solutions.

Mr. PICKERING remarked that there were very strong positive arguments in favour of the hydrate theory, and that his opponents had in no way controverted them. Even if they succeeded in refuting all the objections which he had raised against the physical theory, this theory could not be established till it was shown that other theories were either untenable or less satisfactory.

The freezing-points of sulphuric acid solution calculated by Arrhenius certainly showed a very striking agreement with the observed values; but, before attributing much weight to this agreement, it would be necessary to examine carefully the details of the calculations, for there are considerable sources of doubt and difficulty in applying the values for the conductivity of weak sulphuric acid solutions; but even if no exceptions could be taken to the calculations, it must be remembered that the agreement exhibited extended only up to 1 per cent solutions, or 0.4° depression, whereas, according to the values quoted above, his theory offered an equally good agreement up to 30 per cent, or 34° depression, and, according to values given elsewhere, a similar agreement extended, with certain exceptions, up to 94 per cent. It must also be remembered that according to the chemical as well as the physical theory there must be a mathematical connection between the freezing-points, conductivities, and all other properties of solutions. The freezing-point curve shows irregularities, and so also does the conductivity curve; the chemical theory explains these irregularities, whereas according to the physical theory they should not exist.

Professor van 't Hoff pointed out that according to his theory the freezing-points were influenced by the nature of the solvent; but this does not remove the objection that the nature and amount of the dissolved substance (even when this is a non-electrolyte) are found to influence the results. Professor van 't Hoff had misunderstood what had been said about Raoult's constant. He (Mr. Pickering) was well aware that this constant and that deduced in the osmotic pressure theory were quite different.

Professor Ostwald stated that his experiment of bringing a charged body up to a solution, dividing the latter and removing the charged body was precisely analogous to a similar operation performed on a metallic conductor instead of a solution. This is undoubtedly the case, but in both instances there is an expenditure of mechanical energy, for more work must be done to remove the charged body from the separated and now charged solution or conductor than was required to bring it up to it; energy has been expended, and as a result we get a current and a certain amount of chemical decomposition: how can this prove that the substance was decomposed to start with? All that it could prove seemed to be that a current developed by electrostatic induction produced the same results both qualitatively and quantitatively as an ordinary galvanic current—a fact which has been established long ago.

Considerable stress has been laid on the constancy of the heat of neutralisation as an argument in favour of the physical theory, but it must be remembered that this constancy has received an equally simple explanation on the hydrate theory.

At the conclusion of the discussion Dr. GLADSTONE remarked upon the satisfactory circumstance that by means of the meeting of the British Association scientific men

had been brought together from the Continent and various parts of England who held diametrically opposite opinions upon the subjects discussed, but that there had ensued a *rapprochement* and mutual understanding which could not fail to render the views of both sides more accurate representations of fact.

As the meagre ten minutes allotted to each speaker in the above discussion did not give time for the expression of all that appears above, some of the statements therein contained are new to me, and I may perhaps be allowed to supplement my answer by a few further remarks.

The bone of contention between Professor Arrhenius and myself, as to whether strong solutions possess an abnormally low or high freezing-point, is easily removed, for we are using "strong" in a different sense, he meaning solutions containing 5 to 10 per cent of the dissolved substance, of which the freezing-point is generally abnormally high; I in the sense of the strongest solutions (of any easily soluble substance) from which the solvent can be frozen, and of which the freezing-point is in most known cases abnormally low, the increase in the molecular depression exhibited by them amounting to from about 6 to 45,600 per cent. Twelve instances, which Professor Arrhenius seems to have overlooked will be found in the *Phil. Mag.*, xxx., pp. 499-501. It certainly appears to be somewhat disingenuous of Professor Arrhenius to pretend that I could have been ignorant of the fact that moderately strong solutions of sulphuric acid show a smaller molecular depression than very weak ones, for it is my own observations which have established this fact, and to it I have twice especially alluded (*loc. cit.*, p. 499, and *Chem. Soc. Trans.*, 1890, p. 357). It is also remarkable that Professor Arrhenius should be so anxious to show that strong solutions have an abnormally high freezing-point, since he starts by telling us that according to the physical theory the reverse should be the case.

Professor Arrhenius accuses me of neglecting the effect of dissociation when discussing the freezing-points. In this he is quite right, for I do not believe in it; nor do I think that correcting the irregularities of one property (freezing-points) by the irregularities of another (conductivities) can be offered as a legitimate "explanation" of the irregularities in either. Moreover, these irregularities cannot be attributed to the same cause which endows a solution with the power of conducting electricity, for solutions of non-electrolytes (though as a rule they behave more regularly) show in many cases as wide a deviation both from constancy and from regularity as any of those quoted above. One of these, indeed (alcohol), is a so-called non-electrolyte. I shall have occasion to show elsewhere that the freezing-points of sulphuric acid when calculated with the help of the conductivities do not show quite such an absolute agreement with the observed values for very weak solutions, as Arrhenius's table indicates, even if we allow the alteration of Kohlrausch's conductivity value for infinite dilution from 270 to 256, or to any other number apparently selected with the object of making the agreement as good as possible. Professor Arrhenius should have extended his calculations further than he has done; he would then have found that the small negative error between 0.6 and 1 per cent, after becoming a fairly large positive one between 1 and 8 per cent, again becomes negative, and reaches the modest dimensions of 60°.

I do not think with Mr. Shaw that any exception can be taken to the monohydrate of sulphuric acid as a solvent; it is a definite crystalline substance, which separates in a pure condition when a liquid containing it is cooled, just as sulphuric acid or water itself does. Mr. Shaw's remarks about Fig. 1. is due to a want of clearness on my part in describing this figure, which does not represent the molecular, but the total depression.

Professor Lodge misunderstood my criticism of Ostwald's experiment. This would form a perpetual-motion machine only if no energy has been expended in the

decomposition, which is impossible, whereas if energy has been expended the experiment can prove nothing whatever. Our views on this point seem to be identical.

Professor Fitzgerald very truly remarks that the dissociation hypothesis cannot be said to be in contradiction to the conservation of the energy if sufficient hypotheses be made respecting the energy of the ions; but are not these hypotheses themselves in practical contradiction to the conservation of energy (or of matter)? They involve either the introduction of electric charges from nowhere, just when and where we please, which can combine with matter to generate just as much heat as may be convenient to the theory, or else they hypothecate a new form of atom which shall be *minus* that free energy which we must admit an ordinary isolated atom possesses, or at any rate *minus* just so much of it as will suit the theory in question.

Dr. Gladstone's remarks at the conclusion of the debate must have made many of us feel that, however useful these discussions were, they might be much more useful if they were better arranged, if the contributors had more time for preparing their papers, if they had some opportunities of communicating together respecting the arguments to be adduced, if the hour of the debate were more convenient, and if the speeches were not cut short through lack of time. In the present case it was as late as July 29th when (in the middle of a holiday and far removed from all requisite materials) I received the invitation of the organising committee to open the discussion, the paper having to be sent in by some early day in August, if it were to appear in print before the meeting. Then on the day of discussion an interesting paper was introduced just before the hour (11.30) for which the discussion had been advertised to begin, the effect of which was the proceedings did not begin till past noon, and then before one o'clock, and after the opening paper and Dr. Gladstone's paper had been read, the President, naturally preferring the discussion of sandwiches and sherry to that of hydrates and ions, left the chair, having first, however, graciously signified that subsequent speakers, several of whom had come many hundred miles to honour us as our guests, and to expound their own views, might have a whole ten minutes each in which to do the latter. Surely these things might be better managed.—SPENCER U. PICKERING.

THE RELATIONS BETWEEN ATOMIC WEIGHT AND MAGNETISM.

By LEO ERRÉRA.

In a sealed paper committed to the care of the Belgian Academy of Sciences on February 2nd, 1878, and opened in March, 1881, I endeavoured to show that the magnetism of the elements depends periodically on their atomic weight in such a manner that the elements of Mendeleeff's odd series are dia-magnetic, and those of the even series are para-magnetic. The discrepant statements on the magnetic behaviour of simple bodies are to be found in the memoir quoted, collocated at length and inserted in Mendeleeff's well-known table. Certain exceptions were then already taken into consideration, and their possibility was to a certain extent admitted.

Independently of the author, Carnelley arrived in September, 1879, at the same conclusion.

As for the intensity of the para-magnetic and dia-magnetic powers, the author pointed out at the same time that it also was in connection with the periodic system, as it may be easily seen from the elements of the 4th, the 7th, and the 11th series. In consequence of our very imperfect knowledge of the magnitude of those forces I was unable to detect a pervading regularity in this respect. Carnelley was similarly unsuccessful.

Latterly Bachmetieff (*Journal Russian Phys. Chem.*

Soc., xxi., 4, 1889) believed that he had found a general law. He assumes that we obtain an irregularly serpentine curve, alternately ascending and descending by plotting out the atomic weights as abscissæ and the intensities of the positive or negative magnetism as ordinates. This curve would be to a great extent in conflict with the rule indicated by the author and by Carnelley. On examination it is perceived that the Russian physicist has proceeded in an arbitrary manner. Thus he asserts that K, according to Lamy (*Ann. Chim. Phys.*, Series 3, vol. li., 1859, p. 305), is dia-magnetic, whilst Lamy maintains the very opposite. Ti, Pd, Os, Pt are placed by Bachmetieff as dia-magnetic, though Faraday found them to be para-magnetic. As regards platinum, Bachmetieff certainly appeals to the statement of Kokscharoff (1867); but for this body Faraday's observation is certainly correct, since subsequent experiments by Mouton (1878) confirm its para-magnetic character. And as the metal employed by Mouton had been prepared by Stas, and declared to be pure and free from iron, it may be maintained that the para-magnetic character of platinum is fully established. This sufficiently shows the incorrectness of Bachmetieff's curve. It evidently does not agree with demonstrated facts as well as the conjectural rule proposed by Carnelley and the author.—*Berichte der Deutsch. Chem. Gesellschaft*, Vol. xxiv., No. 1, p. 88.

DETECTION AND DETERMINATION OF VERY SMALL PROPORTIONS OF ALUMINIUM IN CAST-IRON AND STEEL.

By ADOLPHE CARNOT.

THE author takes a rather large quantity of the metal, for instance 10 grms., and attacks it with hydrochloric acid in a platinum capsule. The use of glass or porcelain is avoided as much as possible to prevent any accidental introduction of alumina from the apparatus.

When the metal is entirely dissolved, without allowing the solution to become peroxidised by exposure to the air, it is diluted with distilled water and put into a flask or a beaker, washing it several times by decantation, and retaining the insoluble portion—graphite, silica, &c.—upon a filter. A portion of silica may remain in solution, and must be eliminated afterwards; but this must not be done by evaporating the solution to dryness, as it contains an enormous quantity of ferrous salt.

The greater part of the free acid is neutralised with ammonia and then with sodium carbonate, and sodium thiosulphate is added. When the violet colouration has entirely disappeared and no more ferric salt in the solution, which is now completely colourless, he adds 2 or 3 c.c. of a saturated solution of sodium phosphate and about 20 c.c. of a solution of sodium acetate. The liquid is then heated and raised to a boil, which is kept up for about forty-five minutes, as long as the slightest odour of sulphurous acid is perceived.

There is formed a precipitate, generally of little bulk, consisting of aluminium phosphate mixed with sulphur, and containing a little silica and ferric phosphate. This precipitate is received on a filter and washed with a little boiling water, and then placed on a capsule of platinum and treated in heat with 10 or 15 c.c. of hydrochloric acid diluted with water.

The solution is evaporated to dryness, and the residue is kept at 100° for an hour, so that the silica may become perfectly insoluble in acids. It is then re-dissolved in a little dilute hydrochloric acid, heat being applied to redissolve all the aluminium and iron phosphate; the liquid is filtered to remove the last traces of silica, diluted with 100 c.c. of cold water, and the precipitation of the aluminium phosphate is repeated by the same method—that is, by almost complete neutralisation of the acid with sodium carbonate, the addition of thiosulphate in the cold, and subsequently of a mixture (previously dissolved)

of 2 grms. acetate and 2 grms. thiosulphate, boiling for half an hour, and filtration through a small filter of paper, which has been washed with acids and leaves no ash.

The silica and the small quantity of iron which remained in the first precipitate have thus been completely eliminated from the second, which, after having been washed with boiling water, is dried, ignited, and weighed.

The aluminium phosphate thus obtained ($\text{PO}_5\text{Al}_2\text{O}_3$) contains 22.45 per cent of aluminium. The operation requires only a few hours, and gives accurate results.—*Bull. de la Soc. Chim. de Paris*, Vol. v., No. 3, p. 139.

STUDIES ON THE EARTHS OF THE CERIUM AND YTTRIUM GROUP.*

By A. BETTENDORFF.

(Continued from p. 159).

LANTHANUM ammonium nitrate is much disposed to form supersaturated aqueous solutions, from which crystals operate only on prolonged standing. It is therefore advisable, as Auer von Welsbach observed, to induce crystallisation by means of small crystals of the salt when it ensues very rapidly. After a few series of crystallisations, systematically conducted, we obtain colourless transparent lanthanum-ammonium nitrate in large crystals. If examined by daylight, both the crystals and their aqueous solution are perfectly colourless; but by gas or petroleum light they both show a rather strong rose-red colour. The solution, in fact, displays then a strong absorption spectrum of didymium. If we proceed to a further purification by separating out the greater part of the double salt by a number of successive crystallisations, removing the mother-liquor and again proceeding in the same manner with the solution of the crystals, we obtain a series of mother-liquors, first of a faint rose-colour, then yellowish-green, and lastly colourless. From the last-mentioned, pure lanthanum-ammonium nitrate separates out in large crystals, colourless both by daylight and lamplight. The concentrated solution shows no trace of absorption lines in a stratum of 0.1 m.m. in thickness. A comparative spectroscopic examination of the various mother-liquors to which the author returns below, showed that this manner of treatment effected a separation of Auer von Welsbach's neodymium and praseodymium. The ammonium double salt of the latter earth is evidently less soluble and adheres more firmly to the corresponding lanthanum salts. It is interesting that the salts when mixed in certain proportions give crystals and solutions which appear perfectly colourless by daylight, but in which neodymium may be at once recognised by gas light.

The explanation of this phenomenon, as well as of the fact that all the didymium salts and their solutions appear of a more intense rose-colour by gaslight than by daylight is to be found in the mutual action of complementary colours, and the poverty of the gas-flame in those rays of light which are absorbed by neodymium.

In his research on the decomposition of didymium into its elements, Auer von Welsbach found in the spectrum of praseodymium four absorption bands which are shown in the illustration accompanying his memoir as gradually decreasing in intensity and breadth towards the red end of the spectrum. Unfortunately they have not been reduced to wave-lengths, but by comparing the designs for didymium and its components it is easily found that the bands $\lambda 5917$ and 5871 , and then $\lambda 4813$, $\lambda 4687$, $\lambda 4453$, must belong to praseodymium.

The absorption spectrum of the author's second mother-liquor showed the three bands last mentioned extremely intensified, while the groups of lines in the yellow part of the spectrum was much enfeebled with the exception of

* From *Liebig's Annalen*.

the bands $\lambda 5815, \lambda 5692$. In the seventh mother-liquor this behaviour was more clearly visible. Of the band $\lambda 5917$, which was to be the only characteristic of praseodymium in the yellow, nothing remained; the band $\lambda 5871$ was faint, but $\lambda 5815-\lambda 5723$ appeared fairly intense. The spectrum of the twelfth mother-liquor had only indications of the above-named groups in the yellow; $\lambda 5765$ was almost as sharp as a hair. The eighteenth mother-liquor displayed merely the bands $\lambda 4813, \lambda 4687, \lambda 4452$.

This behaviour is seen most plainly if the mother-liquors are compared spectrophotometrically, care being taken that equal quantities of the absorbent substance are traversed by the source of light. The quantity of absorbent substance was so selected for the band $\lambda 4813$, which is equally sharp on both sides that it shows the same intensity and breadth in all comparisons.

The intensity and the breadth of the absorption bands vary, as it is well known, according to the contents of the absorbent medium. They are, as Bunsen showed for the salts and solutions of didymium, equally great if the equal quantities of absorbent matter are presented to the light on its way. If we call l and l' the lengths of the strata traversed, d and d' the quantity of didymium oxide in the volume unit of the solid or liquid substance, the conditions for a comparative examination are fulfilled if $1.d = l.d'$. If in two solutions of didymium both l and d are known in one, and if the second is placed in a hollow prism, and if we compare the spectra projected above each other in a suitable manner, the thickness of the stratum l' may be so varied by displacing the prism that both spectra display, for didymium compounds of the same origin an identical appearance as concerns the number, the breadth, and the intensity of the absorption bands.

For didymium compounds of different origins this does not hold good for all bands, as Nilson and Krüss have observed in a number of cases. In their investigations they were led to the conjecture that Auer von Welsbach's neodymium and praseodymium must be mixtures of different earths. As regards the latter component of didymium this suspicion has proved correct.

For comparative spectrophotometric determinations the author uses a small hollow prism, made from a thick-sided glass tube of 0.02 m.m. internal diameter. It was melted off round at one end, and at the other drawn out and cut off like a combustion tube. The glass vessel thus prepared, about 0.09 m.m. in length, is ground off prismatically in such a manner that at the rounded end there remains in the middle only 0.002 thickness of side. Thus is formed the glass frame-work of a hollow prism which is closed by cementing on with Canada balsam two thin glass slips, such as are used for microscopic covering glasses.

The hollow prism is mounted in such a matter that it can be moved to and fro before the slit of the collimator of the spectroscope, and the thickness of the stratum traversed can be read off on a scale. A small instrument supplied by the mechanic Max Wolz, of Bonn, is eminently adapted for obtaining, in systematic fractionated precipitations or decompositions of the earths which yield absorption spectra, a speedy decision on the intensities of the several bands.

As a source of light the author uses, according to the example of Linnemann, the light of zirconia ignited in the oxy-hydrogen blowpipe. In addition to its unusual intensity this light contains a number of violet rays, so that this part of the spectrum appears brightly illuminated, and longer than with gas or petroleum light. With the best lamps the author has been able to effect sharp measurements of the absorption-bands up to $\lambda 4240$, but with the zirconia light it is easy to extend the measurements as far as $\lambda 4100$.

(To be continued).

Professor Corfield has been elected an Honorary Member of the Imperial Society of Medicine of Constantinople.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

March 19th, 1891.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

Messrs. William Ramsay, Spencer Umfreville Pickering, and Edgar J. Millard were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edward Arthur Barnes, 57, Delafield Road, Charlton, S.E.; Frederick Arthur Evans, Cape Colony, South Africa; Joseph Fitze, 1, New China Bazaar Street, Calcutta; Walter Herbert Joseland, 9, Campbell Grove, Oxford Road, Manchester; John Wild, 28, Hyde Road, Woodley, Stockport.

The following papers were read:—

18. "*Molecular Refraction and Dispersion of Various Substances.*" By J. H. GLADSTONE, Ph.D., F.R.S.

This paper contains a record of a considerable number of hitherto published observations of refractive indices that had accumulated in the author's note book, together with the optical constants calculated from them, and remarks on their bearing on chemical or physical theory.

Observations are quoted on carbon bisulphide and benzene at various temperatures which confirm the old conclusion that the specific refractive energy of a liquid is a constant not affected by temperature.

In a second series of tables the data are recorded relating to a number of carbon compounds mostly prepared by Dr. Perkin; the molecular refraction and dispersion calculated from experiment are compared with those reckoned from the values already assigned to the constituent elements. In the majority of cases the experimental and theoretical numbers are in fairly close accordance; in some cases, however, there is a discrepancy larger than is likely to be due to experimental error or impurity of substance. This, of course, points to some difference of constitution. Amongst the comments made upon these results the following may be noted:—The molecular dispersion of amylene shows the amount of increase for double-linked carbons which characterises the allyl compounds previously examined, and the allyl and diallylacetic acids in the table. The three modifications of xylene, while differing considerably in their actual indices, have almost identically the same molecular refraction and dispersion.

Safrol agrees in optical properties with what may be termed the normal value reckoning for four double-linked carbons; but anethoil, cinnamene, and butenylbenzene, though they have only the same number of double linkings, give a refraction, and especially a dispersion, far above what theory requires; thus indicating the presence of carbon in that still more refractive and dispersive condition to which the author drew attention in 1881.

Some of the results, e.g., those relating to the isomeric maleic and fumaric ethers, afford fresh confirmation of the analogy between the molecular refraction and dispersion and the molecular magnetic rotation of the same substance as observed by Perkin.

The nitrogen compounds give results quite confirmatory of the two values previously assigned to that element in combination. The same remark applies to the isomeric ethylic thiocyanate and mustard oil.

The observation of stannic ethide gives a refraction equivalent for tin, 18.1, in fair accordance with that determined from its chloride; but the value of zinc in zincic ethide, 15.9, differs totally from that determined from its dissolved salts.

Observations are also quoted of the halogen compounds of silicon and titanium which tend to confirm the former refraction equivalents, and indicate that the atomic dis-

persion of silicon is very small, about 0.32; and that of titanium very large indeed, about 8.7.

19. "Contributions to Our Knowledge of the Aconite Alkaloids. Part I. On the Crystalline Alkaloid of *Aconitum Napellus*." By WYNNDHAM R. DUNSTAN and W. H. INCE, Ph.D. (from the Research Laboratory of the Pharmaceutical Society).

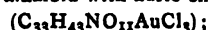
The authors have investigated the properties of a crystalline alkaloid obtained from the root of *Aconitum napellus* by extraction with amyl alcohol, as suggested by the late Mr. John Williams. For a supply of the material they are indebted to the kindness of Messrs. Howard and Sons, of Stratford.

The yellowish indistinct crystals melted at 188.4° (corr.), and by crystallisation from alcoholic solution were proved to be associated with a small quantity of a gummy amorphous base. On combustion, the original substance gave numbers agreeing fairly well with the formula $C_{33}H_{43}NO_{12}$, which is that proposed for aconitine by Wright and Luff (*Trans.*, 1879). The alkaloid was purified by repeated crystallisation from a mixture of alcohol and ether, or more readily by conversion into its bromhydride and regeneration of the alkaloid from the salt, or by regeneration from its crystalline aurichloride. It crystallises in tabular prisms belonging to the rhombic system; the crystallography of the substance forms the subject of a separate communication from Mr. Tutton. The crystals are very slightly soluble in water and light petroleum, more soluble in ether and alcohol, most soluble in benzene and chloroform. They melt at 188.5° (corr.). Contrary to the statements of previous observers, who found aconitine to be *laevo*-rotatory, the authors found an alcoholic solution to be *dextro*-rotatory, $[\alpha]_D + 10.78^\circ$; the aqueous solution of the bromhydride is, however, *laevo*-rotatory, $[\alpha]_D - 30.47^\circ$. On analysis, the alkaloid afforded results which agreed best with the formula $C_{33}H_{43}NO_{12}$.

Two crystalline *aurichlorides* were obtained. One melting at 135.5° (corr.) ($C_{33}H_{43}NO_{12}HAuCl_4$); the other, a basic aurichloride ($C_{33}H_{43}NO_{12}AuCl_3$) melting at 129° (corr.). These compounds are obtained without difficulty, and afford trustworthy means of identifying aconitine. The alkaloid may be readily recovered from them in a pure state.

Aconitine is not appreciably affected by heating at a temperature below its melting-point, but at this temperature it is gradually converted into the uncrystallisable base aconine. Prolonged boiling in aqueous solution induces a similar change, but not to the same extent unless an alkali is present. Boiling with water acidulated with chlorhydric acid also produces decomposition of the alkaloid.

Dehydraconitine or *apo*-aconitine is a base differing from aconitine by the absence of a molecular proportion of water which was first obtained by Wright and Luff by acting on aconitine with acids. Its existence has, however, been questioned by later workers. The authors find that such a substance may be readily procured by heating aconitine with saturated aqueous tartaric acid in closed tubes, as recommended by Wright and Luff. The crystals of this substance melt at 186.5° (corr.). It forms crystalline salts, and in other respects closely resembles the parent alkaloid. The results of analyses agree well with the formula $C_{33}H_{43}NO_{11}$. Three *aurichlorides* were obtained: one ($C_{33}H_{43}NO_{11}HAuCl_4$) melts at 141° (corr.); this salt, when crystallised from aqueous alcohol, affords a hydrate ($C_{33}H_{43}NO_{11}HAuCl_4 \cdot H_2O$), m. p. 129° (corr.), isomeric with aconitine aurichloride, into which, indeed, it very readily changes. The third aurichloride is a direct compound of the alkaloid with auric chloride—



it melts at 147.5° (corr.).

An *amorphous base* was obtained from aconitine, together with benzoic acid, by prolonged heating with water in a closed tube. It appears to be identical with

the *aconine* of Wright and Luff. The same substance is formed together with a resinous substance when aconitine is heated with an alkali. Neither aconine nor its salts could be crystallised. The amorphous base after purification and its amorphous aurichloride afforded analytical data agreeing with the formulæ $C_{26}H_{41}NO_{11}$ and $C_{26}H_{41}NO_{11}HAuCl_4$ respectively.

A further study is being made of aconine, and of the question as to the existence of other alkaloids in this plant.

DISCUSSION.

Dr. ALDER WRIGHT expressed his gratification that the authors so substantially corroborated the results brought before the Society by himself some thirteen years ago. The difference in the results obtained by various chemists he thought was largely attributable to defective methods of isolation of the active principle, whereby the true aconitine became more or less hydrolysed, or otherwise acted on, so as to be transformed into non-crystalline, and comparatively inert, substances; also to the imperfection of the methods adopted for separating the true active crystallisable alkaloid from the non-crystalline and far less active alkaloids naturally accompanying it. It was greatly to be regretted that preparations were largely sold under the name of aconitine, of which only a very small fraction actually was aconitine, the greater part consisting of relatively inert other alkaloids. It was as though a substance should be sold as morphine which almost entirely consisted of narcotine and the other less active opium bases, so that its physiological potency was only a small fraction of that of genuine morphine.

Dr. THUDICHUM forcibly described the uncertainty and danger attending the use of the drug "aconitine" in medical practice, owing to absence of uniformity in the products of English, French, and German manufacture. A final determination of the properties and mode of preparing the active principles of the various kinds of aconite would, he said, be a work of great value.

Professor DUNSTAN, in reply, said it was well known that the commercial aconitines varied much in toxic power, all of them being more or less impure, chiefly from the presence of amorphous alkaloid, which appeared to be non-toxic. Dr. Waller, of St. Mary's Hospital, had undertaken to investigate the physiological action of the pure alkaloid obtained in the course of this research. It was intended to fully examine the alkaloids contained in *A. ferox* and *A. saponicum*.

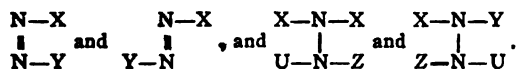
20. "The Crystallographical Characters of Aconitine from *Aconitum Napellus*." By A. E. TUTTON, Royal College of Science, London.

The author has made a complete crystallographical examination of some fine specimens of aconitine crystals, obtained during the course of the work described in the preceding communication. Aconitine crystallises in the rhombic system. Habit: prismatic, with inclination to tabular, owing to the large development of the brachypinacoid. Ratio of axes: $a:b:c = 0.5456:1:0.3885$. Forms observed: $a\{100\}$, $b\{010\}$, $p\{110\}$, $p'\{120\}$, $m\{101\}$, $q\{021\}$, and $o\{121\}$. A complete table of angles is given in the memoir. There is a good cleavage parallel to $a\{100\}$. Optic axial plane is $b\{010\}$. Aconitine is a highly dispersive substance. The apparent acute angle of the optic axes in air 2E for lithium light is $47^\circ 0'$, for sodium light $56^\circ 10'$, and for thallium light $65^\circ 5'$. Hence there is a dispersion of $18^\circ 5'$. The double refraction is positive.

21. "The Asymmetry of Nitrogen in Substituted Ammonium Compounds." By S. B. SCHRYVER, B.Sc.

Although isomeric compounds in which isomerism is due to the different geometrical arrangement of radicles round the carbon atom have for several years been known, stereo-isomers—to use V. Meyer's term—in which the radicles have different arrangements round a nitrogen

atom—have not up to the present been conclusively proved to exist. Hantzsch and Werner (*Ber.*, 23, *et seq.*) have sought to explain the existence of the different hydroxamic acids of Lossen and the mono- and di-benzoxime compounds of V. Meyer and Auwers (*Ber.*, 21, 784) by the hypothesis that they are stereo-isomers of nitrogen: they suppose that this element is capable of forming compounds the general types of which may be represented by the constitutional formulæ—



This explanation of the isomerism is not accepted by Meyer (*Ber.*, 23, 603). Moreover, the evidence of the existence of such stereo-isomers in the case of compounds other than the hydroximes and hydroxamic acids is, up to the present, very slight and of a very doubtful nature.

If, however, the compounds of trivalent nitrogen are capable of forming such stereo-isomers, we should expect that in compounds of pentavalent nitrogen, where the opportunity for difference in the relative arrangements of the radicals in the molecule is greater, stereo-isomers should also, *a fortiori*, exist. To produce these has been the primary object of the author's work.

The class of compounds chosen for study was the substituted ammoniums. The tertiary amines easily combine with alkyl iodides without evolution of heat (under suitable conditions), and it is, therefore, possible to obtain well-crystallised compounds, viz., the platinichlorides, under such conditions that isomeric changes are not likely to take place.

The author, in conjunction with N. Collie, examined the platinichlorides obtained from the different mixed methyl and ethyl ammonium bases of the formulæ Me_2EtNOH , $\text{Me}_2\text{Et}_2\text{NOH}$, MeEt_3NOH ; these were prepared both from triethylamine and also trimethylamine as a starting point. But it did not seem to make any difference in the crystalline form of the platinichlorides, whether the base was prepared from triethylamine or trimethylamine, or whether the solutions were evaporated by the aid of heat or *in vacuo*.

The author has, however, since prepared quaternary ammonium compounds, containing three different radicals:—

- I. By adding methyl iodide to diethylisoamylamine.
- II. By adding isoamyl iodide to diethylmethylamine.
- III. By adding ethyl iodide to ethylmethylisoamylamine.

The platinichlorides of I., II., and III. gave on evaporation by means of heat needle-shaped crystals belonging to the *rhombic system*.

The platinichlorides of I. and II. on evaporation *in vacuo* gave needle-shaped crystals belonging to the *monoclinic system*, whilst III. on evaporation under the same conditions gave needles which resembled those obtained by evaporation by heat.

Further, the monoclinic needles on re-dissolving in hot water on evaporation were changed into the rhombic variety. They were also changed to the rhombic variety by adding excess of chlorhydric acid and allowing the solution to evaporate at the temperature of the atmosphere. From these results the author is led to the conclusion that the difference in crystalline form is due to the various arrangements of the radicals ethyl, methyl, isoamyl, and chlorine around the nitrogen atom, and, therefore, that stereo-isomers are possibly capable of existence in the case of quaternary ammonium compounds.

22. "Acetylcarbinol (acetol), $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$." By W. H. PERKIN, jun., Ph.D., F.R.S.

Some time since the author, in conjunction with Dr. Tingle (*Proc. Chem. Soc.*, 73, 156), succeeded in preparing acetylcarbinol by the hydrolysis of monochloracetone by means of barium carbonate. As, however, the amount obtained by this process is exceedingly small and its iso-

lation extremely laborious, the author has been engaged for some time in endeavouring to improve the method of preparation. The following process was ultimately devised and employed with success in preparing large quantities of pure acetylcarbinol. 200 grms. of acetylcarbinyl acetate ($\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OC}_2\text{H}_5\text{O}$), prepared by digesting monochloracetone with potassium acetate in alcoholic solution, is dissolved in 350 grms. of water heated to boiling, and freshly precipitated barium carbonate added in small quantities at a time until no further action takes place. The clear solution is distilled as rapidly as possible under reduced pressure (100 m.m.) and the distillate, which contains 20 per cent of acetylcarbinol, very carefully fractionated under ordinary pressures with the aid of a long Glinzky column. After repeated fractionation a product is obtained which contains over 90 per cent of acetylcarbinol. This is dissolved in pure ether, thoroughly dried with freshly-ignited sodium sulphate, the ether distilled off, and the residue fractionated under reduced pressure.

Acetylcarbinol boils at $120-122^\circ$ under 250 m.m., and at about 147° under ordinary pressure. When cooled in a mixture of ice and chlorhydric acid it solidifies to a hard crystalline mass; its rel. den. at $15^\circ/15^\circ$ is 1.0795; its magnetic rotation 3.650 .

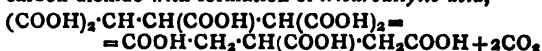
Sodium amalgam converts acetylcarbinol quantitatively into methylglycol, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{OH}$ (b.p. 188°).

23. "The Action of Ethyl Dichloracetate on the Sodium Derivative of Ethyl Malonate." By ARTHUR W. BISHOP, Ph.D., and W. H. PERKIN, jun., Ph.D., F.R.S.

When a mixture of ethyl malonate (2 mols.), sodium ethylate (2 mols.), and ethyl dichloracetate (1 mol.) is digested in alcoholic solution in a reflux apparatus, interaction rapidly takes place with separation of sodium chloride. At the end of two hours, the alcohol was distilled off, the residue mixed with water, extracted with ether, and the oily residue which remains, after distilling off the ether, fractionated under reduced pressure. After repeated refractionation it was ultimately separated into two new compounds, α -ethyl ethylenetricarboxylate, $(\text{CO}_2\text{Et})_2\text{C}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, and β -ethyl propanetricarboxylate, $(\text{CO}_2\text{Et})_2\text{C}\cdot\text{CH}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CH}(\text{CO}_2\text{Et})$.

The former is a colourless peculiar-smelling oil which boils at $203-205^\circ$ (100 m.m.); on hydrolysis, it yields ethylenetricarboxylic acid, and this, on heating to 180° , is decomposed quantitatively into fumaric acid and carbon dioxide.

The latter ethereal salt is an extremely thick oil which boils without decomposition at about 265° under a pressure of 80 m.m. On hydrolysis it is converted into a polycarboxylic acid, probably propanepentacarboxylic acid, as the substance, when heated at 180° , readily loses carbon dioxide with formation of tricarballic acid,—



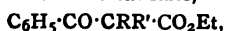
24. "Benzoylactic Acid and some of its Derivatives. Part V." By W. H. PERKIN, jun., Ph.D., F.R.S., and JAMES STENHOUSE.

This research was instituted with the object of supplementing, and in some cases rectifying, the results obtained in investigations previously carried out on the same subject (compare *Trans. Chem. Soc.*, xlv., 170; xlvii., 240; xlviii., 261; xlix., 154).

Ethyl benzoylacetate contains one hydrogen atom which is readily displaced by sodium, and the resulting sodium derivative yields, on treatment with alkyl iodides, the ethereal salts of higher homologues of benzoylactic acid, of the formula $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CHR}\cdot\text{COOC}_2\text{H}_5$.

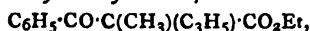
Sodium dissolves readily in ethereal solutions of these derivatives, but, in spite of a large number of experiments, no general method has as yet been found by which di-substituted derivatives of ethyl benzoylacetate (similar to those obtained from ethyl acetoacetate) can be prepared. When treated with sodium ethylate and alkyl iodides in the usual manner, mono-substituted

derivatives of ethylic benzoylacetate usually yield only traces of di-substituted ethereal salts,—



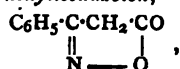
the greater portion being decomposed with formation of benzoic acid, fatty acids, &c.

By digesting ethylic methylbenzoylacetate with sodium ethylate and allyl iodide in alcoholic solution in a reflux apparatus, however, an almost quantitative yield of ethylic allylmethylbenzoylacetate,—

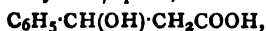


is obtained. This ethereal salt boils at 243–245° (225 m.m.); on hydrolysis it yields quantities of benzoic acid, together with a small quantity of a ketone, probably allylmethylacetophenone.

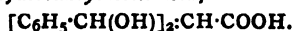
Action of Hydroxylamine on Dibenzoylactic Acid.—Dibenzoylactic acid and hydroxylamine readily interact in alkaline solution, with formation of a substance, $C_6H_5 \cdot NO_2$, which, on examination, was found to be identical with the phenylisoxazolone,—



obtained by Claisen (*Ber.*, xxiv., 140) by the action of hydroxylamine on ethylic benzoylacetate. When heated with phenylhydrazine at 180°, ethylic dibenzoylacetate is completely decomposed with formation of benzoylphenylhydrazine, $C_6H_5 \cdot CO \cdot NH \cdot NH \cdot C_6H_5$. On reduction, dibenzoylactic acid yields β -phenyllactic acid,—



and dihydroxydibenzoylactic acid,—



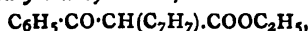
This new acid crystallises from water in slender glistening needles which melt at 188–190°.

Ethylic methyl dibenzoylacetate,—



is prepared by the action of benzoyl chloride on the sodium compound of ethylic methylbenzoylacetate. It is a thick oil which is much less stable than ethylic dibenzoylacetate and is almost entirely decomposed on hydrolysis with formation of quantities of benzoic acid.

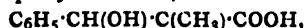
Ethylic benzylbenzoylacetate,—



prepared by heating together ethylic benzoylacetate, sodium ethylate, and benzyl chloride in alcoholic solution, is a thick light-yellow oil boiling at 265° (80 m.m.).

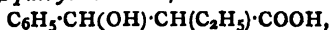
Benzylacetophenone, $C_6H_5 \cdot CO \cdot CH_2 \cdot CH_2 \cdot C_6H_5$, is obtained by the hydrolysis of the previous compound. It crystallises from alcohol in glistening plates which melt at 70°. It is converted by hydroxylamine into the hydroxime $C_6H_5 \cdot C(NO)H \cdot CH_2 \cdot CH_2 \cdot C_6H_5$, which melts at 80–81°. Reduction with sodium in moist ethereal solution converts benzylacetophenone into diphenylpropyl alcohol, $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot C_6H_5$, a thick colourless oil which boils at about 240° (70 m.m.).

α -Methyl- β -phenyllactic acid,—



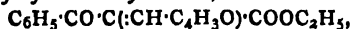
obtained by reducing ethylic methylbenzoylacetate with sodium amalgam, melts at 95° (not at 124–125°, as previously stated, *Trans. Chem. Soc.*, xlix., 160). When heated at 280°, it is decomposed with evolution of carbon dioxide and water and formation of methylstyrolene, $C_6H_5 \cdot CH:CH \cdot CH_3$ (b. p. 174–175°).

α -Ethyl- β -phenyllactic acid,—



is obtained by the reduction of ethylic ethylbenzoylacetate with sodium amalgam. It crystallises from bisulphide of carbon in needles which melt about 108°.

Ethylic furfuralbenzoylacetate,—



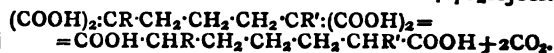
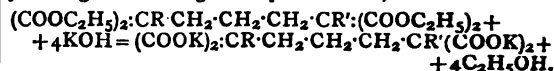
is prepared by heating a mixture of furfural, ethyl benzoylacetate, and acetic anhydride at 180°. It crystallises from methyl alcohol in beautiful glistening prisms which melt at 68°.

25. "Syntheses with the aid of Ethyl Pentanetetra-carboxylate." (Preliminary Note). By W. H. PERKIN, jun., Ph.D., F.R.S., and BERTRAM PRENTICE.

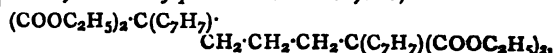
Ethylic pentanetetra-carboxylate (*Trans. Chem. Soc.*, li., 241) yields a disodium derivative,—



from which by the action of alkyl iodides, higher homologues may be obtained, and these, on hydrolysis and subsequent splitting off of two molecules of carbon dioxide, yield higher homologues of pimelic acid,—

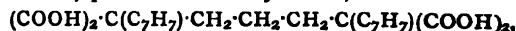


Ethylic dibenzylpentanetetra-carboxylate,—



prepared by the action of benzyl chloride on the disodium compound of ethyl pentanetetra-carboxylate, is a solid crystalline substance which melts at 75–77°.

Dibenzylpentanetetra-carboxylic acid,—



obtained by the hydrolysis of the above ethereal salt, is a colourless crystalline substance, very sparingly soluble in ether. It decomposes at 207–210° into dibenzylpimelic acid and carbon dioxide. The silver salt, $C_{23}H_{20}Ag_4O_8$, is a white powder, insoluble in water.

Dibenzylpimelic acid,—



crystallises from a mixture of benzene and light petroleum in well-formed glistening prisms which melt at about 117°. The barium salt, $C_{21}H_{22}O_4Ba + 3H_2O$, is more soluble in cold than in hot water, and separates, when the cold saturated solution is heated to boiling, in colourless plates.

26. "The Oxidation of Mannitol by Nitric Acid. α -Mannosaccharic Acid." By T. H. EASTERFIELD.

The recent researches of Emil Fischer and his pupils have shown that, whereas mannose is almost quantitatively converted into mannitol on reduction, dextrose yields mannitol with difficulty; hence it appears probable that dextrose and mannitol are not so directly related as has been supposed, and that as mannitol and mannose are easily converted, the one into the other, their relationship is a very close one; it therefore was to be supposed that mannitol, like mannose, would yield mannosaccharic and not saccharic acid, on oxidation with nitric acid. The author, at Professor Fischer's suggestion, has experimentally investigated this question, and his results completely confirm the correctness of the theoretical argument.

Mannosaccharic acid yields no sparingly soluble acid potassium salt; and it readily affords a double lactone.

Specific Odour of Soil.—MM. Berthelot and André.

—The peculiar and not disagreeable odour given off by arable soils when recently moistened, e.g., by a short shower, is well known. The authors find that the essential principle of this odour resides in a neutral organic compound of the aromatic family, and which is carried away by the vapour of water, as is the case with bodies possessing a feeble tension. Its proportion is exceedingly small, and may be regarded as some millionths.—*Comptes Rendus*, cxii., No. 12.

CORRESPONDENCE.

ATOMIC WEIGHTS.

To the Editor of the Chemical News.

SIR,—I have read with some interest the reply which my note on Atomic Weights has called forth from Mr. A. E. Johnson.

Mr. Johnson's contention—as I understand him—is, that he is quite right in retaining the erroneous weight for platinum, since the correct weight leads to an incorrect factor in calculating potash analyses, &c. This statement is, of course, in accord with Dittmar and MacArthur's results; for they point out that it is unsafe to assume that the precipitate of the double chloride consists of the theoretical PtR_2Cl_6 ; and they further seem to suggest that every analyst should determine his own factor by experiments on pure salts of potassium, &c.; since, by so doing, he would get a factor certainly correct for his own mode of working. But, of course, admitting all this, I cannot admit that it is advisable to state a wrong atomic weight in a table of weights; and it appears to me that Mr. Johnson, in the next edition—which will doubtless be very soon required—of his handbook, should correct the atomic weight of platinum, and call attention in a footnote or elsewhere to the experiments of Dittmar and others on the determination of the factor to be taken.

With regard to the closing paragraph of Mr. Johnson's letter, I may point out that as the revised weights for the members of the platinum group now cause these elements to appear in the order which is demanded by deductions from the Periodic Law, it is pretty certain that no considerable readjustments of the weights will be found necessary.—I am, &c.,

F. H. P. C.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxii., No. 12, March 23, 1891.

This issue puts on record the regrettable death of M. Cahours, which took place on the 17th ult. The deceased became a member of the Chemical Section in 1868, having been elected as successor to Dumas.

Action of Heat upon Carbon Monoxide.—M. Berthelot.—Carbon monoxide persists, even at the most elevated temperatures, and its gaseous density remains constant, sensibly identical with that of nitrogen up to about 4000°, according to experiments on gaseous explosive mixtures. Yet this stable compound gives signs of decomposition, with production of traces of carbon and of carbon dioxide, at much lower temperatures, such as at a bright red, according to H. Sainte-Claire Deville, and even at dull redness, according to the author's former observations. He does not accept the hypothesis that we have here a phenomenon of dissociation, since charcoal, &c., is not the true element C, but a polymer of lower or higher rank. Hence charcoal never appears as the direct result of decompositions effected at low temperatures. Whatever is the temperature employed, the proportion of carbon monoxide decomposed varies little, whether at 500°, or at moderate redness, or at bright red heat. But at a full or even a moderate red heat there are deposited at the extremities of the tube two distinct rings of carbon, whilst at 500–550° not the least trace of a carbonaceous deposit is to be seen. Hence the decomposition is preceded by polymerisation.

On a Reaction of Carbon Monoxide.—M. Berthelot.—This gas reduces ammoniacal silver nitrate. The reagent was prepared by adding to a dilute solution of silver nitrate dilute ammonia drop by drop so long as the precipitate formed at first re-dissolved completely. If a few bubbles of carbon monoxide are passed into this solution, it quickly turns brown, even in the cold, and at a boiling heat it gives at once a very abundant black precipitate. This reaction is a new approximation between carbon monoxide and the aldehyds.

A Contribution to the Physiology of Parasitical Plants.—A. Chatin.—The author proves that a parasite growing on plants of the *Strychnos* genus contain neither strychnine nor brucine. The mistletoe growing upon the oak does not contain the blue tannin of the latter, but exclusively a green tannin. In like manner, other parasites are shown not to absorb the peculiar principles of their hosts.

Action of Hydriodic Acid upon Silicon Chloride.—A. Besson.—Dry hydriodic acid is without action on silicon chloride at ordinary temperatures. At elevated temperatures, we obtain partial substitution products. The author obtains $\text{Si}_2\text{Cl}_3\text{I}$ as a colourless liquid which distils at 113–114° and does not solidify at 60°. It is decomposed by water and by exposure to air and light. A second chloriodide, $\text{Si}_2\text{Cl}_2\text{I}_2$, accompanies the former in small quantities. It distils at 172°, and is also decomposed by water.

Transformation of Sodium Pyrophosphate into Phosphite.—L. Amat.—The author examines the conditions of this change, namely, the influence of dilution, of the proportion of acid and of the kind of acid. The hydrochloric and nitric acids act the most energetically, the sulphuric and the phosphorous less so, and the acetic acid least energetically of all the acids examined.

On Platinum Bromonitrites.—M. Vèzes.—The series of bromonitrites includes the platonitrite, the platibromonitrite, the platibromonitrosnitrite, and the bromoplatinate.

The Disaggregation of the Neutral Salts of Amines of the Fatty Series by means of Water.—Albert Colson.—The salts of the amines capable of restoring the blue colour of litmus which have been reddened by the mineral acid with which they have been combined, are decidedly dissociated by water, even about 50°.

New Compounds of Pyridine.—Raoul Varet.—The compounds formed are the pyridine bromozincate, bromonickelate, bromocuprate, argentiodide, and argentic bromide. The argentic chloride, if it exists, is not stable at the ordinary temperature. The affinities of the haloid salts of silver for pyridine decrease from the iodide to the bromide and the chloride, the inverse of what takes place with ammonia.

Theory of the Phenomena of Dyeing.—Léo Vignon.—All the phenomena of dyeing necessitate two essential conditions:—The presence of acid or basic functions in the material to be dyed; the presence of the same functions in the colouring matters. The sole exception of this rule is that of the tetrazo colouring matters, which are taken up by cotton without a mordant, in an alkaline bath, and which will require a special study. We are entitled to say that the phenomena of dyeing obtained with soluble colouring matters are of a purely chemical order, and that the rules of chemical action are sufficient for their explanation.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Fancy Soaps and Perfumery.—A correspondent desires the name of the most recent work on this subject.

An Explosion.—Could any of your correspondents explain the following:—One evening, while getting my lantern ready for exhibition, I had attached the tubing to the oxygen cylinder, but found it was leaking at the coupling. I had to re-adjust this several times, and, of course, each time turning on and off the gas; the last time I turned it on, the regulator, which was of the bellows pattern, or exactly like an oxygen bag, exploded with a very loud report equal to a 4-horse gun, accompanied with a flash of light at least 15 inches in diameter. I at once turned off the gas, but in the few seconds a portion of the metal was fused. Now there was no light nearer than the gas-light in the hall 10 feet off—and we know oxygen is not inflammable of itself—nor was the hydrogen turned on; so what could have caused the explosion with combustion? No doubt pressure would have caused the collapse of the regulator, but whence the fire? Unless there was friction, the fire must have come from within.—H. D. B.

MEETINGS FOR THE WEEK.

- MONDAY, 13th.—Medical, 8.30.
Society of Arts, 8. "The Decorative Treatment of Natural Foliage," by Hugh Stannus, F.R.I.B.A.
TUESDAY, 14th.—Institute of Civil Engineers, 8.
Royal Medical and Chirurgical, 8.30.
Photographic, 8.
Royal Institution, 3. "The Geography of Africa," by J. Scott Keltie, F.R.G.S.
Society of Arts, 8. "Decorative Plaster Work: Stucco Work," by G. T. Robinson, F.S.A.
WEDNESDAY, 15th.—Meteorological, 7.
Microscopical, 8.
Society of Arts, 8. "The Sources of Petroleum and Natural Gas," by Wm. Topley, G.R.S.
THURSDAY, 16th.—Royal, 4.30.
Royal Society Club, 6.30.
Institute of Electrical Engineers, 8.
Chemical, 8.
Royal Institution, 3. "Recent Spectroscopic Investigations," by Prof. Dewar, M.A., F.R.S.
FRIDAY, 17th.—Quekett, 8.
Physical, 5. (1) "On a Property of Magnetic Shunts," by Prof. S. P. Thompson. (2) "An Alternating Current Influence Machine," by James Wimshurst.
Royal Institution, 9. "Magnetic Rocks," by Prof. A. W. Rücker, M.A., F.R.S.
SATURDAY, 18th.—Royal Institution, 3. "The Dynamo," by Prof. Silvanus P. Thompson, D.Sc., B.A.

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THE CHEMICAL NEWS.

VOL. LXIII., No. 1638.

ON THE CAUSE OF THE ODOUR EMITTED BY THE SOIL OF A GARDEN AFTER A SUMMER SHOWER.

By Dr. T. L. PHIPSON, F.C.S., &c.

THIS subject, with which I was occupied more than twenty-five years ago, appears from a paragraph in the last number of the CHEMICAL NEWS (vol. lxiii., p. 176) to have recently attracted the attention of Professor Berthelot and M. André. I find, on referring to my old notes, which are dated 1865, that it is doubtful whether I ever published the results of these observations, and as the distinguished chemists I have just named have not quite solved the problem, I hasten to give the results I obtained so long ago.

After a considerable number of observations, I arrived at the conclusion that the odour emitted by soils and sedimentary strata after a heavy shower of rain in summer was due to the presence of organic substances closely related to the essential oils of plants, and it appeared evident to me that, during the hot dry weather, these porous surfaces absorb the fragrance emitted by thousands of flowers, and give it up again when the rain penetrates into these pores and displaces the various volatile substances imprisoned therein, which are only very slightly soluble in water. I believe that many kinds of soil possess this property, but those on which my observations were first made were the chalk soils of Picardy, in France. I found that not only chalk, but also marls, compact limestones, phosphatic rocks, and some kinds of schists and amphibolites are porous enough to possess it to such a degree as to emit a decided odour when they are strongly breathed upon.

Finding the property of which I speak very remarkable in certain chalk rocks of Picardy, I endeavoured to ascertain the nature of the substance, or substances, to which it was owed. I dissolved a very large quantity of the chalk in dilute hydrochloric acid, and passed the carbonic acid through various media, water, alcohol, weak potash solution, and dilute acid; but none of these liquids appeared to arrest the passage of the odoriferous substance. The only liquid which I found would retain it was an aqueous solution of bromine. This arrested it, and when the bromine solution was afterwards carefully evaporated at a low temperature, a yellowish product, soluble in alcohol, and having a strong odour of cedar wood, was obtained, which, from its chemical and physical properties, appeared to be very similar to, if not identical with, bromo-cedren, derived from essence of cedar.

THE VOLATILITY OF HYDROGEN SULPHATE AT THE ORDINARY TEMPERATURE OF THE AIR.

By ARTHUR COLEFAX, B.A.

IN the CHEMICAL NEWS (vol. lxiii., p. 151) there appeared a paper by G. A. Koenig entitled "Is Sulphuric Hydrate Volatile at the Ordinary Temperature of the Air?" In this communication Mr. Koenig records an observation which has come under his notice pointing to an affirmative answer to the question his paper proposes. Some skeleton crystals of metallic iron had been placed on a watch-glass, supported on an iron triangle in an ordinary

desiccator containing hydrogen sulphate, and had after nine months become coated with a white crust of anhydrous ferrous sulphate.

In the course of my work on phenuvic acid (*Four. Chem. Soc.*, March, 1891, p. 190) I made some curious observations in connection with the neutral body obtainable from this acid by elimination of carbonic acid. Schloesser (*Annalen*, 250, p. 223) had noticed that a portion of the white crystalline solid placed over hydrogen sulphate in a desiccator had, in twenty-four hours, become for the most part, liquid. I submit a short account of some experiments made, in the hope of gaining information as to the nature and cause of this change, which seemingly bear out Mr. Koenig's experience.

A portion of the white crystalline neutral body (phenyl methylfurfuran, according to Paal) which had remained quite unchanged in the air for three weeks, was placed in a perfectly clean desiccator over pure sulphuric acid. The substance (about $\frac{1}{2}$ grm.) was in the centre of a large watch-glass, supported on a glass triangle. In four hours, the previously white crystalline neutral body had become brown and slightly moist, and in twenty-four hours was dark brown and quite moist. Other portions of the same sample of neutral body were then placed over different drying agents, with the following results:—

Over Phosphoric Anhydride no change was observable after fourteen hours.

Over Calcium Chloride no change after the same length of time.

In order to ascertain whether the rapid change over hydrogen sulphate was due to impurities in the acid, the two following experiments were made:—

A quantity of the neutral body exposed over calcium chloride in a desiccator in which was a small vessel containing a solution of sulphur dioxide showed, even after twenty-four hours, no tendency to change.

To a solution of potassium nitrite in water, in which a small quantity of the neutral body was suspended, sufficient hydrogen sulphate was added to evolve traces of hydrogen nitrite. The experiment was made in a small glass stoppered cylinder. Even after many hours no change was noticeable.

This rapid change over sulphuric acid was not an isolated occurrence. I noticed it always when I placed any of the neutral body in a desiccator containing pure sulphuric acid. The desiccator was never exhausted; the experiments were made at the ordinary pressure.

NEW METHOD FOR THE DISCOVERY OF FAINT SPECTRAL BANDS.

APPLICATION TO THE SPECTRUM OF THE HYDROCARBONS.

By H. DESLANDRES.

THE band-spectrum attributed to the hydrocarbons or to carbon alone is furnished by the sources of light most commonly used; it is also found in the solar spectrum and constitutes to a great extent the spectrum of comets and of a certain class of stars. Its importance is therefore very great.

The author has studied this spectrum by a novel method which enables him to complete it and to add to it with certainty three new bands, *i.e.*, λ 438.19, λ 437.13, λ 436.5. These bands are not given by the combustion of the hydrocarbons, but they accompany the ordinary bands of the hydrocarbons and of cyanogen in the electric arc, and in the combustion of cyanogen. They were consequently at first, *e.g.*, by Liveing and Dewar, ascribed to this latter gas.

Now, the application of the general law of the distribution of bands which the author proposed (*Comptes Rendus*, 1887) for the spectra of bands, enables us to conclude that the bands in question belong certainly to the group of the

Spectra of the Hydrocarbons in Numbers of Vibrations.									
SERIES I.		SERIES II.		SERIES III.		SERIES IV.		SERIES V.	
N.	Interval.	N.	In.	N.	In.	N.	In.	N.	In.
								167'94	14'97
								182'91	
						166'61	15'17		
						181'78			
		163'39	15'64	165'09					
161'59		179'03	15'92	180'18	15'39				30'54
177'48	15'89	194'95	16'14	196'15	15'67			213'45	
193'60	16'12	211'69		212'08	15'92	212'87	31'09	229'09	16'64
				228'21	16'13	228'76	15'89		

hydrocarbons. This application is summarised in the following table, which shows these three bands and the sixteen known bands of the hydrocarbons arranged in five series, in which the intervals of the bands, according to the law, increase in arithmetical proportion: the series being, moreover, superposable. The bands, expressed in the numbers of vibrations, are arranged in the five perpendicular series, so that the equal intervals of the series are on the same horizontal line. At the points of a series where a band is wanting, the interval is equal to the sum of the corresponding intervals of the other series.

According to this table, we may, with the sixteen known bands, on setting out with seven of these bands find by calculation exactly the nine others. On carrying out the calculation under the same conditions we obtain the three bands in question, which in numbers are represented by N 228'21, N 228'76, N 229'09. These three bands belong to the groups of the hydrocarbons.

We may even, by carrying out the calculation further, obtain the position of bands still more refrangible, e.g., $\lambda = 408'35$ and $\lambda = 408'17$. But, according to all analogies, these bands must be very faint and lost in the very strong bands of the cyanogen group.

However this may be, by adding the three new bands the group of the hydrocarbons, considered as a whole, takes a form more systematic and regular, and approximates more closely to the band spectra of nitrogen, the only ones which have as yet been studied in a complete manner. These various spectra, as their study is carried sufficiently far, approach a common uniform type, the constancy of which is due to the similar variations of the whole numbers which govern them.

This application of the law of the distribution of bands forms a new method for the discovery of faint bands which are lost in a mixture of groups of different bands. It is the first instance of the discovery by calculation of new bands in band-spectra.—*Comptes Rendus*.

STUDIES ON THE EARTHS OF THE CERIUM AND YTTRIUM GROUP.*

By A. BETTENDORFF.

Concluded from p. 173).

THE plates of zirconia first used by Linnemann were prepared by means of strong pressure and fixed in small platinum plates. They require to be very carefully handled in order to be moderately permanent. Dr. W. Kochs, a tutor in this University, succeeded in fritting this infusible earth by a peculiar treatment, and moulding it permanently into any desired form. He found cylinders of 0'02 m.m. in length and 0'008 m.m. in diameter most convenient for illumination. I am indebted to his kindness for a number of such cylinders, which, along with the small accompanying oxyhydrogen lamp, can be obtained at a very moderate price from the mechanician Wolz, of Bonn.

* From *Liebig's Annalen*.

As already remarked, the last mother-liquor obtained in purifying the lanthanum-ammonium nitrate—the 23rd—showed no trace of absorption lines, and the crystallisations previously separated out were perfectly pure lanthanum-ammonium nitrate. This double salt which was first obtained by Sainte-Claire Deville, and was optically and crystallographically examined by Descloizeaux, leaves on ignition perfectly white lanthanum oxide, which was dissolved in nitric acid, precipitated with pure oxalic acid, ignited again, and served for a series of determinations of equivalents, O = 15'96, S = 31'98.

1. 0'9146 grm. lanthanum oxide yielded 1'5900 grm. lanthanum sulphate.
2. 0'9395 grm. gave 1'6332 grm.
3. 0'9133 " 1'5877 "
4. 1'0651 " 1'8515 "

1. Equivalent RO = 108'14; $R_2O_3 = 324'42$
2. " " = 108'15; " = 324'45
3. " " = 108'15; " = 324'45
4. " " = 108'16; " = 324'48

Hence the atomic weight of lanthanum may be calculated as R 92'19 or R^{III} 138'28. P. T. Cleve in his last determinations made it R^{III} 138'22.

It seemed to the author not superfluous to examine the spark spectrum of the lanthanum chloride obtained from the oxide to become certain of its identity with other oxides of lanthanum previously obtained. The monoprismatic spectroscope used for this purpose had, as I believe, been standardised according to the method first indicated by Angström and Thalén, and subsequently used by Lecoq de Boisbaudran, G. Krüss and Nilson, by determining the position of a great number of the Fraunhofer lines as well as of the lines of the metals. The wave-lengths of these lines were taken from the measurements of Angström and Thalén, which are given in M. Kaiser's text-book. For the production of the sparks there was used a Ruhmkorff's coil, a small Leyden jar, and a Bunsen battery of four elements. The striking distance of the sparks was 0'01 metre. The solution of lanthanum chloride was placed in a small glass tube placed vertically, and closed at both ends with corks through which a platinum wire topped with a conical carbon could be made to slide. The lower carbon cone was fixed so that its base just dipped into the solution of lanthanum. In this manner there was obtained a lanthanum spectrum of extraordinary brightness and permanence. For comparison the author gives the measurements of R. Thalén as taken from M. Kaiser's manual.

Thalén, who conducted his experiments with an apparatus of higher dispersion, gives also a great number of lines the values of which are intermediate between those quoted. In general the wave-lengths found agree well with Thalén's figures, and bear witness to the accuracy of the author's spectral apparatus. Still there remain some discrepancies which need explanation. Thus among Thalén's values, as quoted by Kaiser, the lines $\lambda 824$, $\lambda 4655$, and $\lambda 4086$, are printed in large figures as

Thalèn.		Thalèn	
Λ6393	Λ6393	Λ4797	Λ4796
6294	6294	4738	4739
6248	6249	4688	4687
5807	5807	4667	4668
5794	5794	4652	4655
5765	5761	4630	—
5599	5599	4604	4605
5535	5534	4558	4558
5504	5502	4522	4522
5455	5455	4430	4430
5376	3376	4384	4383
5340	5340	4354	4354
5302	5301	4330	4330
5182	5183	4295	4295
5152	5156	4286	4286
5122	5122	4238	4238
5113	5114	4196	4196
4920	4920	4152	4152
4898	4899	4123	4121
4860	4860	4084	4086
4821	4824	4077	4077
4817	—	4044	4042

main lines. The author had difficulty in finding these lines in his lanthanum preparations. But the line Λ4330, which, according to P. T. Cleve, does not belong to lanthanum, is to be found in Thalèn's preparations as well as in those of the author.

BOILER DEPOSITS.*

By Professor VIVIAN B. LEWES, F.C.S., F.I.C., Associate.

Two years ago I had the honour of reading a paper before this Society on "Boiler Incrustations," in which I traced the formation of the scale, and the causes which led to the precipitation and hardening of the calcic sulphate, calcic carbonate, magnesian hydrate, and other compounds which are usually found to be present, and I pointed out that the scales formed by various kinds of water were so characteristic that one could speak with certainty as to the kind of water from which the incrustation had been formed by an analysis of the scale itself. The analyses given below may be looked upon as typical of the incrustations formed by fresh water, brackish water, and sea water respectively in marine boilers:—

Constituents.	River.	Brackish.	Sea.
Calcic carbonate	75·85	43·65	0·97
Calcic sulphate	3·68	34·78	85·53
Magnesian hydrate.. ..	2·56	4·34	3·39
Sodic chloride	0·45	0·56	2·79
Silica	7·66	7·52	1·10
Oxides of iron and alumina .	2·96	3·44	0·32
Organic matter	3·64	1·55	trace
Moisture.. ..	3·20	4·16	5·90
	100·00	100·00	100·00

From this it is evident we may look upon the incrustation from fresh water as consisting of impure calcic carbonate, whilst that from sea-water is impure calcic sulphate, the brackish water from the mouths of rivers yielding, as might be expected, an incrustation in which both these compounds are present in nearly equal quantities.

The importance of these differences in the deposit formed is very great, as it enables the shipowner to arrive at a conclusion as to the treatment that the boilers have received during the voyage, by examination and analysis

* Read at the Thirty-second Session of the Institution of Naval Architects, March 19, 1891; the Right Hon. the Earl of Ravensworth, President, in the Chair.

of the scale which those boilers contained. Taking, for instance, the case of a ship which uses fresh water both for filling and make-up, it is manifest that on her return to port the scale should be very slight and should consist mainly of calcic carbonate; whilst, if the scale exceeds $\frac{1}{16}$ th of an inch and shows a preponderance of calcic sulphate, it is manifest that such scale could only have been formed by sea-water, either leaking in from faulty condensers or being deliberately fed into the boilers.

The reception you were kind enough to give that paper, and the frequency with which it has been quoted since, lead me to hope that, in continuing and completing the subject, I shall be performing a not unwelcome task.

So far the deposits taken into consideration have been those formed from the impurities natural to the water itself; but with the introduction of high-pressure steam a new and highly dangerous form of deposit has added to the trouble of the marine engineer.

As early as 1878, the collapse of the furnaces of the boilers of the s.s. *Ban Righ* and a similar misadventure in the screw tug *Ich Dien*, with no apparent cause to bring about the damage, caused some attention to be paid in marine circles to the action which had taken place, and the only clue to be found was that a certain amount of oily deposit had formed on the tops of the furnaces, and experiments made by Mr. Dunlop, of Port Glasgow, led to the conclusion that this oil, which had distilled into the boiler from the lubricants used in the cylinder, was so bad a conductor of heat that its formation on the plates allowed them to get superheated, with the result that they were unable to withstand the pressure of steam existing in the boiler, and in this way brought about the collapse.

Similar cases of collapse became frequent after that date, no less than thirty vessels being disabled from this cause during the last few years.

The first case which came under my notice, in which damage to boilers had arisen from this cause, was the case of a large ocean steamer, and through the kindness of Mr. Milton, Chief Superintendent Engineer of Lloyd's, I was able to obtain samples of deposit from all parts of the boilers, and full particulars of the case.

The steamer was a large one trading between Liverpool and Boston, averaged twelve days on the voyage, and was fitted with ordinary compound engines. She had three double-ended boilers, with three plain furnaces at each end, and three combustion chambers in each boiler. The furnaces were plain in one length and connected at the back end to the tube plates, being flanged up inside the chamber, whilst the front end plate is flanged inwards on to the furnace crowns. The furnace crown was $\frac{1}{4}$ -in. plate, and the front bottom plate $\frac{1}{16}$ th, the working pressure being 80 lbs. The boilers are about 5½ years old, and have always been re-filled with fresh water at the end of each run, both at Boston and Liverpool; whilst, as a rule, the waste on the voyage was made up by the use of about 70 tons of fresh water, but during the last voyage sea-water was used for this purpose. Every four hours whilst under steam, 4 lbs. of soda crystals were put in the hot well, making about 2 cwt. during the run, the total capacity of the boilers being about 81 tons. For lubricating purposes about seven pints per day of valvoline were used in the cylinders.

When in port, the boilers were allowed to cool down and the water was run off, and they were swept down with stiff brushes, and were afterwards sluiced out with a hose shortly before being re-filled with fresh water. No trouble occurred with the boilers until five voyages before the final collapse, when some of the furnaces began to creep in; they were stiffened with rings and stays, and on the succeeding voyages the whole of the furnaces got out of shape, one after another. Examination of these boilers clearly showed that they had never been very heavily scaled, as in parts of the boiler where it would have been impossible to get at them to clear them out, no signs of heavy incrustation were to be found, and the

absence of marks of scaling tools also showed that they had never been allowed to get very dirty. On the furnace crowns, where they had collapsed, there was only a slight white scale, not more than $\frac{1}{4}$ th of an inch in thickness, whilst on the bottom of the furnaces there was a brown oily deposit $\frac{1}{4}$ th of an inch in thickness, which in other parts of the boilers increased to between $\frac{1}{4}$ th and $\frac{3}{4}$ th of an inch. I obtained from Mr. Milton samples of the thin scale from the top furnaces, and of the deposit from various parts of the boiler, and also specimens of cut-out portions of the boiler plates, Liverpool water, valvoline, and soda crystals put into feed water, and of all these analyses were made.

The boiler plates were as good as the day they were put in, and showed no structural signs of having undergone any change, whilst the analyses of the Liverpool water and the soda crystals used showed that they could have taken no part in the action which had led to collapse.

I.—Valvoline.

The valvoline on analysis gave:—

Vegetable and animal oil	..	nil.
Mineral oil		100 per cent
Acids (free)		nil.
Boiling-point		371° C.
Specific gravity		0.889

II.—Scale from Furnace.

	From top.	From below.
Calcic sulphate	84.87	59.11
Calcic carbonate	5.90	6.07
Magnesian hydrate	2.83	11.29
Iron, alumina, and silica	2.37	2.85
Organic matter and oil	3.23	19.54
Moisture	0.80	1.14
Alkalis	nil.	nil.
	100.00	100.00

III.—Deposit from Tubes.

	Scale on tubes.	Deposit above scale.
Calcic sulphate	50.92	11.60
Calcic carbonate	4.18	0.82
Magnesian hydrate	14.12	22.21
Iron, alumina, silica, &c.	7.47	9.14
Organic matter and oil	21.06	50.20
Moisture	1.17	4.23
Alkalis	1.08	1.80
	100.00	100.00

IV.—Deposit from Bottom of Boiler.

Calcic sulphate		22.52
Calcic carbonate		nil.
Magnesian hydrate		7.09
Silica, alumina, and iron		34.85
Organic matter and oil		27.95
Moisture		5.79
Alkalis		1.80
		100.00

On careful examination of the organic matter and oil present in these deposits, it was found that quite one-half of it was "valvoline," in an unchanged condition, which had collected round small particles of calcic sulphate.

A consideration of these analyses, at first sight, yields no clue as to the cause of the collapse, the scale upon the furnace tops being not only free from oil, but perfectly harmless both in quantity and quality; but, on going more deeply into the question, it is evident that this scale cannot be in the condition in which it was originally

formed, as the deposits from both top and bottom of tubes, from the bottom of the furnaces, and from the shell of the boiler, are all rich in oily matter; and it is impossible that, during this deposition, the furnace tops could have escaped whilst all other parts of the boiler became coated with it. Experiments, however, reveal the actions which had been at work and led to the formation of the deposit, and its absence upon the injured portions of the plates.

The pressure at which the boilers were worked was 80 lbs., corresponding to a temperature of 155° C., or 311° F., which is so far below the boiling-point of the valvoline that it was evident that it had not distilled over in the ordinary way, and experiments were made to see if it could be distilled in steam at a lower temperature. A retort containing valvoline was carefully heated over a sand-bath, its temperature being ascertained by a thermometer, and steam was then blown through it, with the result that at 248° F. or 120° C. the steam became "greasy" and the oil commenced to pass over with it.

This experiment is, I think, important, as it shows that in testing the capabilities of a lubricant, the fact that it has a boiling-point well above the temperature of the steam is no guarantee that none of it will find its way into the boiler. Having thus entered the boiler, the minute globules of oil, if in great quantity, coalesce to form an oily scum on the surface of the water, or, if present in smaller quantities, remain as separate drops; but show no tendency to sink, as, their specific gravity being 0.889, they are lighter than the water, and the difference in gravity is probably even greater at the temperature existing in the boiler.

Slowly, however, they come in contact with small particles of calcic sulphate and other solids separating from the water and sticking to them; they gradually coat the particles with a covering of oil, which in time enables the particles to cling together or to the surfaces which they come in contact with. These solid particles of calcic carbonate, calcic sulphate, &c., are heavier than the water, and as the oil becomes more and more loaded with them, a point is reached at which they have the same specific gravity as the water, and then the particles rise and fall with the convection currents which are going on in the water, and stick to any surface with which they come in contact—in this way depositing themselves, not as in common boiler incrustations, where they are chiefly on the upper surfaces, but quite as much on the under sides of the tubes as on the top, their position being regulated by whether they come in contact with the surface whilst descending or ascending.

The deposit so formed is a wonderful non-conductor of heat, and also from its oily surface tends to prevent intimate contact between itself and the water. On the crown of the furnaces this soon leads to over-heating of the plates, and the deposit begins to decompose by the heat, the lower layer in contact with the hot plates giving off various gases which blow the greasy layer, ordinarily only $\frac{1}{4}$ th of an inch in thickness, up to a spongy leathery mass often $\frac{1}{4}$ th of an inch thick, which, because of its porosity, is an even better non-conductor of heat than before, and the plate becomes heated to redness, and being unable to withstand the pressure of steam, collapses. During the last stages of this over-heating, however, the temperature has risen to such a point that the organic matter, oil, &c., present in the deposit burns away, or, more properly speaking, is distilled off, leaving behind, as an apparently harmless deposit, the solid particles round which it had originally formed.

Such a deposit is much more likely to be produced with boilers containing fresh or distilled water, as the low density of the liquid enables the oily matter to settle more quickly, whilst with a strongly saline solution it is very doubtful if this sinking-point would ever be reached; it is evident also that when oil has found its way into the boiler and is causing a greasy scum on the surface, the most fatal thing that can be done is to blow off the boilers without first using the scum cocks, because as the water

sinks so the scum clings to the tops of the furnaces and other surfaces with which it comes in contact, and on again filling up with fresh water, it still remains there, causing rapid collapse.

A very remarkable instance of this is to be found in the case of a large vessel in the Eastern trade, in the boilers of which an oil scum had formed. The ship having to stop some days at Gibraltar, the engineer took the opportunity of blowing out his boilers, and refilling with fresh water, with the result that, before he had been ten hours under steam, the whole of the furnaces had come in.

Under some conditions the oil-coated particles coalesce and form a sort of floating pancake, which, sinking, forms a patch on the crown of the furnaces at one particular spot, and under these conditions the general result is the formation of a "pocket."

A curious fact which is worthy of attention is that in most of these oily deposits copper is to be found in considerable quantity. In an analysis of deposit from the furnace of a vessel in which a "pocket" had formed from the above mentioned cause, the scale showed, as in the case already cited, no reasonable cause for the injury at the damaged part of the boiler, whilst the deposit from the under side of the furnace tubes showed clearly the presence of large quantities of oil matters, which were partly combined with copper:—

Constituents.	Scale.	Deposit.
Calcic sulphate	90'354	1'02
Calcic carbonate	1'200	nil.
Ferric oxide	3'200	{ 56'90
Oxide of alumina		{ 2'30
Oxide of copper	nil.	{ 1'90
Magnesian hydrate	2'821	1'80
Organic matter	1'600	{ 10'46
Oil		{ 17'84
Sand, &c.	0'825	7'78
	100'000	100'00

It is a fact that even mineral oils have a considerable solvent action upon copper and its alloys, and it is evident that the copper in the oily deposits have been obtained from the fittings of cylinder and condenser. Fortunately this copper is so well protected by oil that in most cases it is extremely unlikely to come in contact with, and deposit on, the metal of the boiler; but if it did, very serious galvanic mischief would be the result.

The next point I attempted to determine was the effect which these oily deposits had in allowing excessive heating of the plates to take place and retarding the heating of the water. A clean iron vessel was taken, and a known volume of water placed in it, and heated by a carefully regulated Bunsen flame, the water being raised to the boiling-point in ten minutes; this experiment was repeated a second time with the same result, and the vessel was then lined with a coating of deposit found in the bottom of the boilers which had collapsed, and rendered binding by admixture with a small trace more valvoline. This coating was laid on $\frac{1}{4}$ th of an inch in thickness, and the former experiment repeated, the same flame being used and the same volume of water taken, with the result that it took fifteen minutes before the boiling-point was reached, showing that, even if no damage resulted to the plates from over-heating, such a deposit would cause a large increase in the fuel used.

In attempting to ascertain to what extent extra heating of the plate took place from this cause, I employed a series of substances of known igniting and melting-point, raised the water in the various vessels to the boiling-point, and then brought the clean bottom of the vessel in quick contact with the test substance, and took the results as indicating the temperature of the exterior of the plates

Clean vessel—	
Sulphur did not melt	below 115° C.=239° F.
Coated vessel—	
Sulphur melted but did not	
in flame	above 115° C.=239° F.
	below 250° C.=482° F.
Gun-cotton ignited	above 200° C.=392° F.

So that the $\frac{1}{4}$ th of deposit caused with a slow heat a rise in temperature of the plate from under 115° C. or 239° F. to over 200° C. or 392° F. It is manifest, however, that the fiercer the heat the more marked will this over-heating become, and in the next series of experiments the Bunsen flame was replaced by an atmospheric blowpipe, and the temperature attained, tested in the same way as before.

Clean vessel—	
Sulphur did not melt	below 115° C.=239° F.
Coated vessel—	
Gun-cotton ignites	above 200° C.=392° F.
Tin melts	" 228° C.=444'4° F.
Sulphur ignites	" 250° C.=482° F.
Lead melts	" 334° C.=633° F.
Zinc melts (just)	" 423° C.=793'4° F.

Whilst, on replacing the atmospheric burner by an oxy-coal gas flame, I found no difficulty in fusing a hole in the bottom of the vessel, which was made of thin wrought iron plate, showing that a temperature of 1500° C.=2732° F. had been attained, and it is therefore manifest that, with the fierce heat existing in the boiler furnaces, given an oily deposit only $\frac{1}{4}$ th of an inch in thickness, the plates will readily be heated to a temperature at which they are totally unable to withstand a pressure of 80 lbs. of steam, and collapse of the furnace crowns must follow.

The great points to be sought in a good lubricating oil are that it shall be a pure mineral oil, and that its boiling-point shall be well above any temperature likely to be attained in the cylinder. Oils satisfying these requirements can readily be obtained, but users of lubricants must remember that, in order to obtain them free from any constituents of dangerously low boiling-point, expensive processes have to be resorted to, which must of necessity increase the price of the oil, and that it is useless to expect to obtain a really good lubricant at a low figure.

The great advantages of a good mineral oil cannot be too strongly insisted on, and any lubricant containing animal or vegetable oils to give it body should be unhesitatingly discarded.

The mineral oils are not fats, but hydrocarbons—compounds of carbon and hydrogen—and the portions used for lubricants are those left after the more volatile constituents have been distilled off, and they differ widely from animal and vegetable oils, which contain so-called fatty acids, which are liberated from them by the action of superheated steam, and these acids attack iron, copper, and copper alloys with the greatest readiness, forming metallic soaps, which are compounds of the fatty acids with the oxides of the metals, and so cause serious damage to both boilers and fittings.

The animal and vegetable oils, in contact with air, especially when heated, take up oxygen, and become gummy and resinous, and gradually so stiff that frequent cleaning becomes necessary—a trouble entirely avoided with mineral oils.

In dealing with the prevention of such deposits, it seems to me that the most feasible plan is to pass the feed water through a long tube filled with clean coke in pieces the size of walnuts, which would act as a scrubber, and would free the greasy water from the traces of oil, and prevent their going forward to the boiler.

I have already pointed out that the collapse of furnaces from the presence of oily deposits almost invariably takes place in boilers fed with fresh water, and that oil, when it goes into the boiler, floats, because it is specifically

lighter than water, until solid particles of calcium compounds coming in contact with it and imbedding themselves in it so increase its weight, that reaching the same density as the water, it commences to circulate with the convection currents in the water, and is so drawn down, and attaches itself to tubes and furnace crowns, causing, eventually, damage.

In the case of a transatlantic liner using fresh water only, it takes at least four days' hard steaming to bring the density up to $\frac{1}{2}$ nd, whilst if sea water had been used the density would have started at this and would never, after the first few days, have been much below $\frac{1}{2}$ nds, and the oil would have remained as a scum, and would never have reached the furnace crowns.

In my last paper on boiler incrustations I pointed out that it was quite possible to prepare sea water in such a way as to practically prevent any serious deposit forming from it, and the same process would prevent the trouble I have now been describing to you.

In the summer of last year Mr. Biles, who is always to the front when he thinks there is a chance of improving marine engineering, kindly gave me the opportunity of trying the effect of prepared sea water upon a crane boiler at the Naval Construction Works, at Southampton, and, after a few preliminary experiments to determine the best form in which to work the "precipitator," the boiler was worked continuously for a month with water drawn from the Itchen half-an-hour before high tide, at which period analysis showed that the water was to all intents and purposes sea water, plus a fair amount of suspended mud; this, after preparation in the "precipitator," was fed into the boiler, and on opening it in the presence of Mr. Milton, Mr. W. H. Riley, R.N., Mr. Biles, Mr. Gearing, and Mr. Dusanoy, it was found perfectly clean, the surfaces looking as if they had been given the thinnest possible coat of whitewash.

The process employed was to add to the sea water a known quantity of precipitator powder, consisting chiefly of soda-ash; and, having done this in a closed vessel, to heat the mixture by blowing into it waste steam, until a pressure of from 5 to 10 lbs. was created, and under these circumstances practically all the magnesium and calcium salts separate from the water and are easily got rid of by filtering it under pressure into the hot well.

I had proposed in the first case to heat the liquid by blowing the steam through a coil in the precipitator, but practical experiments soon showed that the heating surface was not nearly enough, and so the waste steam was simply blown in, allowance being made in the precipitator for the water due to the condensation.

I also found it aided the reaction to heat the water first just to boiling-point before adding the precipitator power, as under these circumstances the deposit settled more quickly and threw less strain upon the filters.

The precipitator was 6 ft. 4 in. high and 3 ft. in diameter, and held a ton of water, and the time taken from the first running the sea water in to its delivery into the hot well was 1 hour 15 minutes, so that in practice, giving plenty of time between the makes, it would be perfectly easy to prepare 8 to 12 tons in the 24 hours with a small precipitator of the size used.

The prepared water has a density of $\frac{1}{2}$ nd, and may with safety be evaporated until its density is $\frac{3}{4}$ nds, the salts present not crystallising out until a density of from $\frac{5}{8}$ nds to $\frac{7}{8}$ nds is reached.

Professor Doremus, of the College of the City of New York, proposes to use sodic fluoride as a precipitant for the scale-forming constituents of sea water, as a smaller weight is required, and the action is more rapid and more perfect.

The great objection has up to the present time been its cost, but I am informed that this has now been so far reduced as to bring it within the scope of extended commercial use; and, should it be used on a larger scale, the price could be readily brought much lower.

Professor Doremus claims that the precipitation of the

calcium and magnesium salts takes place with very great rapidity, that the sediment shows no tendency to cake or adhere to the sides of a hot vessel, and that it is less bulky than the precipitate formed by soda-ash.

In preparing sea water in the way I have proposed, every precaution must be taken to add slightly less of the precipitant than is necessary to entirely throw down the calcium and magnesium salts, as it is manifestly impossible in practice to guard against small quantities of sea water finding their way into the boiler either from leaky condensers or else being fed in by the engineer during some emergency, and, if under these conditions any excess of the precipitant were present in the boiler, a bulky precipitate would be thrown down and cause trouble, although it would not bind into a solid scale.

There is no doubt that, if Professor Doremus can so reduce the price of sodic fluoride as to enable it to be used for this purpose, it would be of great use, as the fluoride undoubtedly completes its action on the salts of magnesium and calcium more rapidly and thoroughly than the soda-ash, and it would be easier therefore to so regulate the quantity added as to remove, say, five-sixths of the injurious constituents from the sea water without allowing any precipitant to enter the boiler.

In conclusion, I will briefly recapitulate the means which seem to me best adapted for preventing the formation of the dangerous organic and oily deposits I have considered in this paper, and these are:—

I.—Filtration of condenser water through a coke column.

II.—Free use of the scum cocks.

III.—The use of water of considerable density rather than of fresh water.

IV.—The use of pure mineral oil lubricants in the smallest possible quantity.

THE PRECIPITATION OF MANGANESE AS AMMONIUM MANGANOUS PHOSPHATE.*

By ALEXANDER G. McKENNA.

In the determination of manganese in iron ores, it is customary to precipitate the manganese as dioxide, after separation from the sesquioxides by the basic acetate process, by adding bromine to the filtrate from the acetic acid precipitation. The manganese thus thrown down may be ignited and weighed as manganese proto-sesquioxide, but the results are inaccurate from two causes. Manganese dioxide when precipitated in the presence of sodium or potassium salts always carries down with it some alkali, which appears to be chemically combined with the manganese, since it cannot be removed by the most prolonged washing with water.†

This source of error can be avoided by using ammonium acetate in the basic separation, but in this case the solution must be made alkaline before manganese can be precipitated by bromine, and the separation from calcium is then rendered less sharp.

Another objection to the determination of manganese based on the ignition of the precipitated dioxide is the uncertainty of the resulting oxide, which is generally assumed to be Mn_2O_3 . Pickering‡ has shown that the percentage of manganese in this oxide varied between 69.69 per cent and 75 per cent, according to the temperature of ignition and other causes.

It is now customary to re-dissolve the manganese dioxide in hydrochloric acid, and then precipitate it as ammonium manganous phosphate. The precipitate is ignited and weighed as manganese pyrophosphate. This method of determining manganese, which we owe to

* From the *Technology Quarterly*, Vol. iii., No. 4, November, 1890.

† See Wright and Menke on Manganese Dioxide, in the *Journal of the Chemical Society* for 1880, p. 23.

‡ *CHEMICAL NEWS*, vol. xliii., p. 226.

Dr. Wolcott Gibbs, is now generally admitted to be the most accurate as well as the most easily performed of all the methods of determining manganese. It has been variously modified by many chemists, but none of these modifications seem to possess any advantages over the original process as given by Dr. Gibbs.

The following work was undertaken at the suggestion of Dr. T. M. Drown, to determine if some of the proposed changes in the details of the process were of any advantage in simplifying the method or enhancing its accuracy.

Two solutions of manganous chloride were prepared, and measured portions were taken for precipitation. In the first method, Gibbs's original directions were followed.* The precipitation was made in a platinum dish, by adding a solution of sodium hydrogen phosphate in excess. The white precipitate which formed was dissolved in hydrochloric acid, the solution heated to boiling, and ammonia added in excess. The solution was now boiled for ten minutes and allowed to stand near the boiling-point for one hour. It was filtered hot, and washed with hot water.

In the second method, Blair's† directions were followed. The solution was made acid with hydrochloric acid, an excess of sodium hydrogen phosphate added, the solution brought to boiling in a platinum dish, and ammonia added drop by drop, with constant stirring, until further addition of a drop of ammonia made no change in the silky character of the precipitate; a dozen drops more of ammonia were added, and after boiling a minute longer the solution was cooled in ice water before filtering. The wash water used was made by dissolving 10 grms. of ammonium nitrate in 100 c.c. of slightly ammoniacal water.

The chief object in view in the third method was to discover if there is any valid objection to making the precipitation in glass, and also to determine the length of time required for complete precipitation. To the solution of manganese salt in a beaker, hydrochloric acid and sodium-hydrogen phosphate were added. The solution was heated to boiling, and 20 c.c. ammonia water added. The boiling was continued three minutes, with constant stirring, which is absolutely necessary to prevent bumping. The wash water used was made by adding one volume of ammonia (sp. gr. 0.96) to three volumes of water. Following are the results obtained in this series of analyses:—

Comparison of Results Obtained by the Three Methods.

	Gibbs's original method. Grms.	Blair's method. Grms.	Precipitation in glass and washing with ammonia water. Grms.
Weight of manganese pyrophosphate obtained, first solution	0.4990	0.4997	0.4994
Do., second solution	0.4996	0.4992	0.5007
Do., second solution	0.0897	0.0896	0.0894

Three more determinations were made by precipitation in glass, but the precipitates did not become crystalline in three minutes, and the washings were turbid.

The manganese precipitates after ignition were examined for silica, but none was found.

This set of experiments seems to show that essentially the same results are obtained by following either Gibbs's or Blair's directions; also that glass is not attacked by the solution in three minutes' boiling, but that this time is not always sufficient to ensure the complete conversion of the precipitate to the crystalline form which is necessary before filtration.

Another series of experiments was made in the same manner, but with a different amount of manganese.

Second Series of Results.

	Gibbs's method. Grms.	Blair's method. Grms.	In glass, as before. Grms.
Weight of manganese pyrophosphate obtained	0.2415 0.2427 0.2408 0.2432 0.2355*	0.2432 0.2432 0.2385 —* —*	0.2412 0.2427 0.2425 0.2387*

* Not crystalline.

These results confirm those in the first series, and indicate the necessity of having the precipitate thoroughly crystalline.

The amount of manganese in the filtrates and washings of each set of these experiments was determined (except in those cases where the precipitate was not crystalline) with the following results. The total volume of the filtrate and washings was in each case about 300 c.c.

Solubility of the Precipitate.

	Gibbs's method. Washed with water. Average grm.	Blair's method. Washed with dilute ammonium nitrate. Average grm.	In glass. Washed with dilute ammonia. Average grm.
Filtrate contained metallic manganese	0.0005	0.0004	—
Washings contained metallic manganese	0.0005	0.0012	0.0003

In order to determine the relative values of the three wash waters under precisely the same conditions, about three times the usual amount of manganese was precipitated by Gibbs's method, and the precipitate was divided into approximately equal parts by pouring alternately on three filters. The precipitate in each filter was washed thirty times, 7 c.c. of wash water being used each time.

The following results were obtained in two experiments:—

Solubility of Precipitate. Second Series.

	In hot water. Grm.	In ammonia (1:4). Grm.	In ammonium nitrate. Grm.
Washings contained metallic manganese	0.0012 0.0018	0.0019 0.0016	0.0024 0.0014

These results show that, if there is any preference, it is in favour of hot water.

On washing with ammonia water, the precipitate is changed in colour to a dark gold, which change does not occur with either of the other wash waters.

Another set of nine determinations was made in glass by boiling the solution, with constant stirring, for eight minutes, or until the precipitate seen through the walls of the beaker had a peculiar silky appearance, resembling that of mercurous chloride when precipitated from a mercuric salt by stannous chloride. The precipitate was washed with hot water.

Results of Precipitation in a Beaker and Washing with Hot Water.

	Grm.	Grm.	Grm.
Weight of manganese pyrophosphate obtained	0.2450 0.2445 0.2440	0.2445 0.2443 0.2443	0.2450 0.2445 0.2442

No silica could be found in any of the precipitates after ignition.

In one experiment iron was present in small amount with the manganese. The precipitated phosphate had a beautiful gold colour, and on being washed with dilute ammonia dissolved gradually in the wash water, giving a brown coloured filtrate. Continued washings showed no diminution in the amount dissolved. On standing ex

* *Am. Jour. Sci.*, [II.], vol. xlv., 216.

† *The Chemical Analysis of Iron*, p. 93.

posed to the air for several hours, a brown precipitate settled out from the wash water. This would seem to indicate the formation of some double salt of manganese and iron, which is soluble in ammonia when an excess of an alkaline phosphate is not present.

(Since the above was written, there has appeared in the *School of Mines Quarterly*, Vol. xi., No. 4, a paper on the same subject, by Mr. R. C. Boyd, which confirms, in general, the results given above).

NOTICES OF BOOKS.

The Evolution of the Elements: a Sketch of a Biogenetic Foundation for Chemistry and Physics. (Die Entwicklung der Elemente: Entwurf zu einer biogenetic Grundlage für Chemie und Physik). By GUSTAV WENDT. Berlin: Hirschwald.

THAT elemental evolution—the necessary complement of our accepted interpretations of the phenomena of astro-geny and organogeny—has been for some time “in the air” is almost a truism. The old theory of some seventy odd simple bodies, all supposed primordial, independent and incapable of mutual conversion, fails to satisfy the inquirer. We crave to know how they have arisen; why their number and their mutual relations are as we find them. Attempts have been already made to answer these questions. The evidence in favour of the non-primordial character of the elements has been carefully marshalled. A principle, the survival of the most inert, has been suggested as likely to play a part similar to that of the survival of the fittest in the organic world. The author of the present memoir goes boldly forward. He contends that the chemical elements are not present in all other worlds in the same number as we find them at our feet. It is not by accident that a certain number have met together with us, another, *e.g.*, on Mars, and some few in the nebulae. Each of the heavenly bodies has a number of elements exactly corresponding to its present stage of development. Or, as he otherwise puts it, the chemical elements are gradually formed during the evolution of the stars and planets. He raises the question whether it might be possible here upon our earth to produce the conditions for several atomic combinations of identical atoms, and thus convert elements into each other. But he does not reply in the affirmative. He suggests that the art of making gold will probably never be learnt, but perhaps some day iodine may be made out of bromine.

Herr Wendt even ventures to construct a genealogical table of the elements, and to fix their possible number. He considers that “the elements in the earth have been formed so that from the seven fundamental elements two series each of seven elements have been gradually evolved, and that further from each of the 3×7 elements a further series is derived.”

The fundamental elements are hydrogen, lithium, glucinum, boron, carbon, nitrogen, and oxygen. The next seven elements, fluorine, sodium, magnesium, aluminium, silicon, phosphorus, and sulphur, form a second complete series. Herr Wendt objects to the practice of placing hydrogen alone as a quite exceptional element, and beginning the first series of the elements with lithium. He doubts the propriety of classing it as an electro-negative element. He objects to several of the details of the arrangement of the elements in the periodic system as formulated by Mendeleeff and Meyer. Thus he transfers chrome from the “oxygen” to the iron group, and proposes to fill up the vacancy in the latter group by the insertion of Websky’s “idunium.” The author protests against the position attributed by Lothar Meyer to copper, *i.e.*, between sodium and silver. From a consideration of its properties he transfers it to the iron group.

The vacancy between sodium and silver he assigns to

Dr. Phipson’s “adunium,” which, hitherto, like idunium, has not been by any means generally recognised.

As regards the possible number of the elements, Herr Wendt pronounces the maximum number, $11 \times 7 + 2 = 79$, the minimum 74, and the mean about 77. Hence, it would seem that he can scarcely accept the resolution of didymium into neodymium and praseodymium, and still less the highly complex (or mixed) character of cerium and others of the rare earths, to which, indeed, he makes no reference. He considers that if the determinations of Grünwald are found trustworthy on further extension this *savant* will have rendered a morphology of the elements possible.

Whilst fully agreeing with the author as regards the genesis of the simple bodies by a process of evolution, we are not able for the present to accept his limitation of their number. This point we should prefer to leave for decision by the *a posteriori* method of spectroscopic and micro-chemical research. Nevertheless, we think that Herr Wendt’s work is entitled to the most careful study of every chemist who is really concerned about a truly rational development of his science.

Mixed Metals or Metallic Alloys. By ARTHUR H. HIORNS, Principal of the School of Metallurgy, Birmingham and Midland Institute. London: Macmillan and Co.

THE author begins his work with a historical introduction, a classification of metals, and some remarks on their general properties. We regret having once more to point out an erroneous atomic weight attributed to platinum, *viz.*, 197.4. After a variety of other preliminary matter, mostly of a very useful character, Mr. Hiorns begins the study of alloys with the metallic compounds of copper. Here he remarks that “pure copper has never been cast in considerable quantity so as to produce a good ductile casting free from blowholes.” An elaborate account is given of the effect exerted upon copper by the admixture of small quantities of other metals. An extensive table shows the properties of recognised copper-zinc alloys to the number of 144, showing their analytical composition, specific gravity, colour, tenacity, ductility, malleability, hardness, fusibility, and conductivity for heat and electricity. Under the last head many blanks remain to be filled up.

Bronzes are next discussed in a very comprehensive manner, including a table of copper-tin alloys. The proportion of phosphorus in phosphor-bronze must not exceed 4 per cent. A table published by the Phosphor-Bronze Company is appended, with the remark that the absence of the statement of the composition of the alloys robs it of its chief value. Silicon bronze is considered superior to phosphor-bronze in its electric conductivity, and has entirely replaced it for telegraphic purposes. Of the aluminium bronzes, that with 10 per cent of aluminium is considered the best.

As regards the alloys of tin and lead, the author ventures upon the hazardous statement that an alloy containing 18 per cent of lead is quite harmless in vessels for wine and vinegar! The alloys of silver and steel examined by Faraday and Stoddart do not present any practical interest. Mr. Hiorns may be congratulated upon the fact that he has produced the best manual of alloys to be met with in the English language.

Action of Chlorine upon Methylene Acetone.—D. Vladesco.—It may be admitted for the present that there are formed by the limited action of chlorine upon methylethyl acetone in the cold, two chlorine derivatives—methyl- α -chloroethylketone and methyl- α -dichloroethylketone. These derivatives are capable of giving rise to bodies with multiple functions, alcoholic and ketonic. The author proposes to continue the study of these compounds.—*Berichte der Deutsch. Chem. Gesell.*, v. No. 3.

CORRESPONDENCE.

THE FELLOWSHIP OF LEARNED SOCIETIES.

To the Editor of the Chemical News.

SIR,—I venture to ask that you will allow me to trespass on your space so far as to offer some remarks on a subject that has lately given rise to no little controversy and discussion among the Fellows of at least two leading scientific Societies, viz., the Chemical and the Linnean.

To readers of the CHEMICAL NEWS it is of course well known that it has, for many months past, been a subject of complaint among the Fellows of the Chemical Society that improper persons have obtained admission who have no real interest at all in science, no qualifications entitling them to the honour of Fellowship, and whose only object in joining was to obtain the powers of writing F.C.S. after their names, thereby stamping themselves among the lay world as qualified chemists; and furthermore—*turpissime dictu!*—using this assumed qualification for trading purposes. We all know that this feeling has given rise to some agitation among the Fellows, and has brought on a mild epidemic of blackballing at the ballots.

At the annual meeting Dr. Russell referred, at considerable length, to this controversy; and in a speech that, as all must admit, abounded in good feeling and conciliatory spirit, expressed his views to this effect: that the Fellowship of the Chemical Society was not, neither was it intended to be, any mark whatever of qualification; that the Institute of Chemistry was open to all who wished to obtain a diploma stamping them as competent chemists, whilst the F.C.S. signified nothing at all; that so far from being exclusive or insisting on evidence of qualification he would wish to see the Society open to all—including even mere amateurs—who might be desirous of joining, always provided that candidates were personally unimpeachable, and were not joining for the sake of obtaining an F.C.S. to be used for trade purposes. In a word, Dr. Russell—as I understand him—would make the F.C.S. as meaningless and valueless as any evidence of chemical knowledge as would be the "Fellowship" of, for instance, the Society of Arts.

Before discussing this position let me refer to the Linnean Society. Here, too, a somewhat similar complaint has been made, viz., that certain persons have obtained the Fellowship simply with the intention of advertising themselves as F.L.S. for trade purposes. It was proposed at a recent meeting of the Linnean Society to limit the number of Fellows annually elected to 30, with the object of electing only the most fit and proper persons. This proposition (which was thrown out) gave rise to a somewhat warm discussion; on the one hand it was contended—just as by Dr. Russell—that the Fellowship was in no sense a diploma, or had no academic value; that the Royal Society existed for the purpose of honouring scientific workers, and that it was very undesirable for any other Society to erect itself into a quasi degree-granting body; let the Fellowship be open to all persons who wished to join, provided always that they were personally unobjectionable. On the other hand, it was contended, *inter alia*, that the Fellowship of the Linnean was an honour, and should not be lightly lavished.

Having thus stated the quarrel may I—without incurring the charge of presumption—venture to express a criticism? I cannot agree with Dr. Russell and others that the Fellowship of such Societies as the Chemical and the Linnean is not an honour or qualification. I cannot admit that—always if merited—it is other than an honour; and it seems to me that it should be so granted as to mark a man as possessing a *competent knowledge* of chemistry or biology, respectively. That it should possess any of the rigid precision of a London degree I do not for a moment contend, but simply that

it should be given only to those who can show that they have earnestly studied and acquired a thorough grounding in the branch of science concerned. Neither can I follow Dr. Russell's argument that the existence of the Institute of Chemistry precludes the Chemical Society from giving any status by granting its Fellowship; and this, for two reasons: firstly because the Institute of Chemistry, which was founded in order to give every competently trained chemist an opportunity of stamping himself with its diploma, has persistently stultified itself by resolutely refusing even to inquire into a candidate's knowledge unless he have required that knowledge in one particular way; and secondly, because there is no such institute of biology, or of geology, or of astronomy; and, I take it, that whatever ruling applies to the Fellowship of the Chemical Society applies equally to that of the sister societies. I conclude, therefore, that the Fellowship of any scientific society confers, and should confer, to a certain extent, a mark of qualification; and if this be denied, and it be contended that the Fellowship is *quite* meaningless, I would ask what in the name of common sense would be the logic of a man's writing F.C.S. for F.L.S., or F.G.S., &c., after his name? No perfectly sane person would dream of writing himself as a Fellow of the Society of Arts, or of the Numismatic Society, or of the Royal Institution, simply because in all these cases it is perfectly understood that there is no sort, kind, or condition of qualification necessary for election to the "Fellowship"; whereas it has always been understood that no one without competent scientific knowledge can obtain the Fellowship of the scientific societies.

In the next place I fully admit that the other societies should make no attempt to arrogate to themselves the functions of the Royal; the analogy and reference seem to me unfortunate and misleading, since the functions are so very different. The function of the Royal Society is to honour *original research* and *this only*, not to signalise merely acquired learning; whereas my contention is that the Fellowship of the other societies should mark simply *competent knowledge*—thorough studentship that is—and most emphatically *not* in any way imply original work. I think this distinction very important, since at the recent meetings of the Chemical and the Linnean several speakers were knocking their heads against this desired or disclaimed analogy to the Royal.

But if the foregoing position be admitted, now comes the difficulty that, it seems to me, might be met by acting on these lines. It is contended that for want of information the societies cannot justly confer their Fellowship in this discriminating way, and also that many students would thus be shut out from the use of the libraries, the Journal, and the meetings of the Societies. Exactly so; and my suggestion is, use your power of electing *associates*: admit them at a lower subscription and without entrance fee; give them the privilege of using the library and attending the meetings, and *emphatically forbid them from writing themselves A.C.S. or A.L.S., &c.* In a word, open the associateship, *without limit*, to all students who wished to avail themselves of the great educational advantages given by membership of these societies, and at the same time prevent them from using their privilege as a qualification. It seems to me that this would, to a very great extent, meet the difficulty under which Fellows at present lie; for in very many cases they must either blackball a candidate, which is not pleasant, or elect as a Fellow one of whose qualifications they are very sceptical. This reformed procedure would irretrievably shut out all those who at present join simply with the intention of using the Fellowship for trade purposes; for these especially are the men who can show no particular evidence of qualification, and who would therefore be required to enter as associates; and it would also meet the case of students who are desirous of using the library and so on, but are not yet sufficiently advanced in their respective studies to be qualified for the Fellowship; and here, I may say, speaking from my own

recollections, that I should have highly appreciated the advantages of the associateship at a time when I should not have felt myself justified in applying for Fellowship; but although the charters of the various societies empower them thus to admit associates, the practice seems almost to remain in abeyance. For instance, the Linnean Society have definitely limited the number of Associates to twenty-five.

I wish it to be understood that I entirely disclaim any desire to make this associateship a necessary preliminary to Fellowship; on the contrary, I hold that anyone who can show that he has completely studied his subject should be elected Fellow forthwith, as at present; but whenever his claims are doubtful, let him be elected associate first. Were he a *bona fide* student he would accept the associateship as a preliminary step; but if he desired the Fellowship for no other reason than to proclaim himself an F.C.S., &c., he would promptly decline it. This procedure would therefore, as it appears to me, exactly meet the case by shutting out the very persons it is desired to exclude, while entailing no hardship at all on the amateurs whom Dr. Russell, in his generous catholicity, wishes to admit to the privilege of the library, the meetings, and the Journal. I may further point out that the adoption of such a course would be a very great relief to Fellows, who are often asked at present to sign certificates for candidates of whom they know nothing; they must either refuse—which is always unpleasant—or else recommend a man of whose qualification they are completely ignorant. But this difficulty would be met if they offered to recommend him for the associateship; then after a year or two's associateship the new comer, if he attended the meetings, would inevitably become known to some of the Fellows, and when he applied for his Fellowship he would have no difficulty in obtaining the signature of Fellows who did personally know him to be a fit and proper person; while, on the other hand, the unfit would quickly find their level.

I must repeat, however, that it is essential to this reform that the writing of A.C.S., &c., be strictly forbidden. Could the method here suggested be adopted, it seems to me that the difficulty would be overcome, and we might admit that the Fellowship of a scientific society was invariably what—as I contend—it should be, and is now, when deservedly conferred, a mark of qualification and an honour. I cannot admit that it is other than an honour, a legitimate source of pride, to be a Fellow of a Society whose roll-call is studded with the names of the leaders of science.—I am, &c.,

F. H. P. C.

P.S.—It is perpetually insisted that the evil now existent might be cured if Fellows would exercise greater care in signing candidate's certificates. Exactly: and if all men were virtuous the world would become comparatively Paradise; but neither consummation is practically probable. But if the distinction between associate and Fellow were prominently brought out, Fellows would certainly become more careful about signing recommendations for Fellowship.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxlii., No. 13, March 31, 1891.

New Method for the Detection of Slight Bands among the Band Spectra. Application to the Spectrum of the Hydrocarbons.—H. Deslandres.—(See p. 179).

On the Origin of the Higher Alcohols in Industrial Phlegmas.—L. Lendet.—The author finds confirmations of his hypothesis that the higher alcohols are for the chief part the products of a secondary fermentation, which, in the earlier part of the operations, is overpowered by the normal alcoholic fermentation.

On Vegetable Hematine.—Dr. T. L. Phipson.—The author concludes that the vegetable hematine described by M. Lenossier in the *Comptes Rendus* (March 2, 1891), is identical with the palmalline, of which he gave an account in the *Comptes Rendus* in 1879. He has observed that the *Palmella cruenta*, formerly known as *Chaos sanguinea*, is sometimes entirely green, and becomes of a blood-red when its vegetation is completed. It is probable that palmelline may be found in various other species of plants.

The Use of Liquefied Carbon Dioxide for the Filtration and the Rapid Sterilisation of Organic Liquids.—A. D'Arsonval.—At high pressures carbonic acid becomes an extremely powerful bactericide. If the pressure is prolonged, and the temperature raised to 40°, no living being can resist.

The Simultaneous Development of Oxygen and Carbon Dioxide among the Cactaceæ.—E. Aubert.—The fact that *Cactus opuntia* gave off oxygen in the light was observed at the beginning of the century by Saussure. Mayor, in studying the *Crassulaceæ*, found that they give off oxygen even in an atmosphere devoid of carbonic acid. The author has since found that certain species of *Cactus*, e.g., *Opuntia tomentosa*, give off in the light at 35° both oxygen and carbon dioxide. In the dark oxygen is absorbed and carbon dioxide liberated. With *Mamillaria elephantideus* the reactions are the same.

Justus Liebig's Annalen der Chemie,
Vol. cclv., Part 3.

On Lactonic Acids, Lactones, and Non-saturated Acids.—R. Fittig.—This continuation includes papers by L. Liebmann, on benzaldehyd and pyrotartaric acid; by Gibson Dyson, on salicylaldehyd and succinic acid; by H. C. Brown, on salicylaldehyd and pyrotartaric acid; and by Johannes Politis, on anisaldehyd and succinic acid.

On Trinitroazoxy- and Trinitroazo-benzoles.—H. Klinger and J. Zuurdeeg.—This memoir does not admit of useful abridgment.

Communications from the Chemical Institution at Marburg.—These include a paper by Th. Zincke and C. Campbell on azimido-compounds, and a memoir by Th. Zincke and Th. Cooksey on tetrachlor- α -diketo-hydronaphthaline and its fusion products, ortho-trichlor-acrylbenzoic acid and phthalylchloracetic acid.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. v., No. 3.

On the Benzene Hexachlorides.—C. Friedel.—This paper requires the accompanying figures.

On Phenanthridine.—Amé Piçet and H. J. Ankersmit.—Phenanthridine appears in the form of long crystals, fusible at 104°. Its properties greatly resemble those of acridine. Its odour is pungent and occasions sneezing. Its salts are yellow, and their aqueous solution has a fine blue fluorescence.

Detection and Determination of very Small Proportions of Aluminium in Iron and Steel.—Adolphe Carnot.—Already inserted.

Action of Soluble Fluorides upon Diastase.—Dr. J. Effront.—Hydrofluoric acid and the fluorides exert a favourable action upon saccharification, not because they

act directly upon diastase, but because they destroy the lactic and butyric ferments.

Preparation of Crystalline Calcium and Barium Fluorides.—H. Moissan.—The former salt is obtained by adding a solution of calcium chloride at $\frac{1}{10}$ th to a boiling solution of potassium fluoride at $\frac{1}{10}$ th. The ebullition is kept up for half-an-hour in the platinum capsule; the product is washed with abundance of water, dried in the stove, and calcined at dull redness. The barium salt is obtained by pouring a solution of 18 grms. barium chloride in 500 c.c. of water into a boiling solution of potassium fluoride at $\frac{1}{10}$ th.

Researches on the Atomic Weight of Fluorine.—Henri Moissan.—The author concludes from three series of determinations that the atomic weight of fluorine is very close upon 19, probably 19.05. The determinations have been made by means of the sodium and the calcium fluorides.

Study of the Fluor-Spar of Quincé.—Henri Becquerel and Henri Moissan.—This fluor-spar contains an occluded gas. All the reactions of the mineral may be explained by the presence of a small quantity of free fluorine in the occluded gases.

New General Method for Iodising Bodies of the Aromatic Series.—M. Istrati.—The author heats the body to be iodised with iodine and sulphuric acid in a flask fitted with an ascending condenser, so as not to lose any volatile products. The author, in a series of papers, applies this method to various aromatic bodies.

Action of Iodine in Presence of Sulphuric Acid upon Calcium Phenylsulphonate.—MM. Istrati and Georgesco.

Action of Chlorine upon Benzene in Presence of Sulphuric Acid.—MM. Istrati and Petricon.

On Pentachlorophenyl Iodide.—M. Istrati.—These three memoirs describe in detail applications of the method proposed by M. Istrati.

New Method for the Preparation of the Non-Saturated Acids of the Aromatic Series.—L. Edeleano.—In a former number of this journal (*Bull. de la Soc. Chim. de Paris*, vol. iii., p. 191), the author described a method for the preparation of cinnamic acid, and he now proceeds to show its general applicability.

New Data relating to the Action of Sulphur Chloride upon Aniline.—L. Edeleano.—The author observes that the products obtained vary not merely with temperature but with the nature of the solvents employed. He obtains a compound, $S(C_6H_4NH_2)_2$, and a resinous matter, the nature of which has not yet been studied.

Series 3, Vol. v., No. 4.

A New Method of Formation of the Derivatives of Indazol.—Otto Witt, E. Noelting, and E. Grandmougin.—This very extensive paper contains an account of nitro-indazol, its methyl-ether, its acetylic derivative, its bromation, oxidation, and reduction. The last operation yields amido-indazol, the salts of which are next described. The memoir concludes with researches on the constitution of indazol.

Studies on the Derivatives of the Toluquinoides and the Xyloquinoides.—E. Noelting and E. Trautmann.—A very lengthy treatise incapable of useful abstraction.

On the Addition of Sulphuric Acid to Wine.—M. A. Villiers.—The author, by occasion of a circular sent out by the Minister of Justice to all the "procureurs généraux," seems too disposed to defend "plastering." He admits, however, that plastering in any case introduces into wine a proportion of potassa more considerable than that which ought to be present, and augments the weight of the extraneous matters. It also increases the acidity of the wine.

On the Composition of Commercial Calcium Biphosphate in its Different Forms, and the Preparation of Crystalline Biphosphate.—G. Pointet.—The biphosphate occurs in two forms, the syrupy and the crystalline. Neither of them contains a product corresponding exactly to the formula $CaH_4(PO_4)_2$. The composition of the syrupy biphosphate is by no means uniform.

This number contains very complete biographies of G. Chancel and Eugene M. Peligot.

Journal für Praktische Chemie. New Series, Vol. xlii., Part 1.

On the Origin of Kyanalkines.—R. Schwaize.—This paper is a continuation of the series on the polymerisation of the nitrites. The origin of the kyanalkines from the nitrites and the sodium alcoholates depends on the nature of both these classes of bodies. Only primary alkylcyanides are capable of such a polymerisation. The reaction proceeds most favourably when the alcoholate employed contains the same alkyl, as the nitril phenolates are incapable of affecting the conversion of the cyanethylys and of the other cyanides into kyanalkines.

Remarks on the Memoir of Goldschmidt and Meissler on "Experiments for the Determination of the Constitution of Tautomeric Compounds."—Arthur Michael.—The author considers that the present task of chemistry, in view of the phenomena of Desmotropy, is to ascertain under what conditions one or the other constitution of a desmotropic body is stable, as well as the constitutional changes which such a body undergoes on the replacement of an atom of hydrogen by other atoms or radicles.

Researches from the Laboratory of the University of Freiburg.—These comprise a memoir by Ad. Claus on the constitution of naphthalene, and a paper by C. Willgerodt on the stages of reduction of the nitro-group on the reduction of nitro-azo compounds with alcoholic ammonium sulphide.

Eukairite from Argentina.—J. Fromme.—The mineral in question contains: silver 42.71 per cent, copper 25.47, selenium 31.53; and consequently differs but little from the specimens obtained from Skrikerum in Smaland, as analyzed by Berzelius and Nordenskiöld. It does not contain the trace of thallium found by the last-named chemist.

On the Stereo-chemistry of Isomeric Nitrogen Compounds.—C. Willgerodt.—A controversial paper in reply to the remarks of Hantzsch and Werner.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. v., No. 59.

New Experiments on the Question of the Fixation of Free Nitrogen.—Sir J. B. Lawes and Dr. J. H. Gilbert.—From *Proceedings of the Royal Society*.

Asbestos and its Industrial Applications.—M. Ludzki.—An account of the occurrence, varieties, properties, and industrial applications of asbestos.

Revue Générale des Sciences Pures et Appliquées. Vol. ii., No. 3, February 15, 1891.

Modern Ideas on Thermometry.—Ch. E. Guillaume.—The author admits that metrology, of which thermometry is a branch, is not a science, but a collection of methods, eminently useful to the sciences of observation. He considers that the expansion of hydrogen furnishes the normal thermometric scale.

No. 4, February 28, 1891.

Chemical Equilibria. Part I. Chemical Mechanics, Experimental Principles.—H. L. Chatelier and G. Mouret.—The authors consider chemistry as consisting of two branches: the one, *chemical architecture*, viewing exclusively bodies of a definite chemical composition, and the other, *chemical mechanics*, discussing the intermediate states through which bodies have to pass before reaching a state of final equilibrium. (The scopes of these two branches might be more intelligible if they were named the morphology and physiology of chemistry).

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Joining Grease-proof Paper.—I shall be glad if any reader can inform me what material will join grease-proof paper one piece to another so firmly that they cannot be separated.—J. S.

MEETINGS FOR THE WEEK.

- MONDAY, 20th.—Medical, 8.30.
Society of Arts, 8. "The Decorative Treatment of Natural Foliage," by Hugh Stannus, F.R.I.B.A.
Society of Chemical Industry, 8. "Stoneware and its Application to Chemical Apparatus," by W. P. Rix. "Tanning by Electricity," by Dr. S. Rideal and Mr. A. S. Trotter.
TUESDAY, 21st.—Institute of Civil Engineers, 8.
Pathological, 8.30.
Royal Institution, 3. "The Geography of Africa," by J. Scott Keltie, F.R.G.S.
Society of Arts, 4.30. "China," by Sir Thomas Wade.
WEDNESDAY, 22nd.—Geological, 8.
Society of Arts, 8. "Bimetallism," by Sir Guildford Molesworth.
THURSDAY, 23rd.—Royal, 4.30.
Institute of Electrical Engineers, 8.
Royal Institution, 3. "Recent Spectroscopic Investigations," by Prof. Dewar, M.A., F.R.S.
FRIDAY, 24th.—Physical, 9. "Euphuism—past and present," by The Rev. Canon Alinger.
SATURDAY, 25th.—Royal Institution, 3. "The Dynamo," by Prof. Silvanus P. Thompson, D.Sc., B.A.

TO CORRESPONDENTS.

E. E. H. Thorne.—*Journal of Analytical and Applied Chemistry*, published by E. Hart, Ph.D., Easton, Pa., U.S.A. Price, 3 dols. per annum.

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THE CHEMICAL NEWS.

VOL. LXIII., No. 1639.

A COMPARISON OF THE METHODS FOR THE ESTIMATION OF MILK-SUGAR.

By J. KNOWLES, F.C.S., and J. ARTHUR WILSON.

The estimation of milk-sugar is, in practice, only required in the analysis of milk and milk products, especially in condensed milks, which latter may also contain cane-sugar, and it is with these this paper deals.

The physical method by the polarimeter has not received sufficient attention it undoubtedly deserves, most chemists relying for the determination on the reduction of metallic solution. It is well known that tables have been constructed for the calculation of the chief constituents of milk (proteids, sugar fat) from the total solids and specific gravity, which are said to agree well with the figures got by direct analysis. We may remark, *passim*, that this is or is not the case according to the method employed, especially as regards milk-sugar, although, for instance, the fat determinations calculated come very close to those by the Adams process, which may be regarded as our best method up to the present, and perhaps showing the actual fat contained in milk.

We have compared the following methods for the estimation of milk-sugar on the same samples of milk which were of a poor quality and high in sugar.

1. Estimation by Fehling, weighing as CuO .
2. " " Pavy Fehling, by simple dilution.
3. " " Pavy Fehling, after separation of casein.
4. " " the optical process.

We shall first describe how the experiments were conducted, and then give a table showing the differences between the processes.

Method 1.—It has been shown over and over again that to attempt to estimate milk-sugar in strongly alkaline solution is inaccurate, on account of the destructive action of alkali on milk-sugar; we have therefore taken this into account. 10 c.c. of milk is diluted and faintly acidified by acetic acid, and diluted to 100 c.c. at 60°F . 25 c.c. of the filtered solution is raised to a boil and filtered at once, the filter washed thoroughly till the filtrate measures 100—110 c.c. This is just neutralised and heated to boil, when there is added a slight but decided excess of boiling Fehling solution; boil three to four minutes. Filter, wash by decantation, and on filter dry, ignite, and weigh as CuO . We would mention that collecting the precipitate on asbestos and reduction in hydrogen gives the same results as direct ignition, but direct weighing as Cu_2O invariably gives too low results. Lastly, the reducing power of milk-sugar has been taken as $7\text{CuO} = 1 \text{ mol. lactose}$.

Method 2.—In this process 10 c.c. of milk was diluted to 100 c.c., and poured into an accurate burette, with a long spit, and connected to the flask containing Pavy Fehling solution, which was briskly boiling. A preliminary test was always made, so that after boiling briskly the main bulk of milk was added, and the process finished by drops. We have not adopted the method of working in a current of gas, because we are satisfied that the above process gives the same results if properly carried out. As standard we have taken that 40 c.c. Pavy Fehling is equal to 0.02 glucose, and that 52 of the latter equal 100 of lactose.

Method 3.—This, as regards manipulation, was carried out as before. In the preparation of the milk-sugar solution 10 c.c. of milk was first acidified by acetic acid and diluted to 100, and the determination made on the

filtrate. It will be noticed in all these determinations we have preferred *measured* quantities of milk for the sake of convenience. It has been urged that this is inaccurate, but we find this is not so if the milk be allowed to stand to get rid of air bubbles. The specific gravity was taken by the Westphal balance, and not till at least 24 hours had elapsed.

Method 4.—We shall describe our method of working this process minutely, because it is the one on which we are inclined to place the most reliance. In our first experiments we employed the usual method of precipitation by basic lead acetate on about 70 grms. of milk; subsequently we modified this in order to reduce the errors, and we think with some success. In the first place it is necessary to be sure that the scale of the polarimeter lying between three and seven angular degrees is correct. This can be done by means of standard solutions of pure sucrose, or still better, by the control tube of Schmidt and Haensch.

The following table assumes the normal weight of sugar for the instrument to be 26.048 grms., the weights of chemically pure sugar and the rotation are in divisions.

Division of polarimeter.	Weight per 100 c.c. of CP. sugar.
3	0.779
4	1.039
5	1.298
6	1.558
7	1.817
8	2.078
9	2.337
10	2.597
11	2.857
12	3.117
13	3.376
14	3.637
15	3.896
16	4.156
17	4.416
18	4.676
19	4.936
20	5.196

If other instrument be used, the weight corresponding to these angular degrees must be calculated. We employed, as previously stated in the first trials, the old process of precipitating by basic lead acetate on about 70 grms. of milk as follows:—About 70 c.c. of milk is weighed or measured, and 5 c.c. of basic lead acetate added (1—2), agitated thoroughly, and diluted exactly to 100 c.c. The observation was then taken at about 60°F . in a 200 m.m. tube, using an instrument of the Laurent type. The specific rotation of lactose was taken at 52.5 for the D line. The results from this process are signified in the table as A, in terms of anhydrous milk-sugar in 100 grms. of milk. The results under B were obtained by the following modified method.

50 c.c. of milk is placed in a flask, having a mark on the neck at 57 c.c., 2½ c.c. of basic lead acetate added, then 1 c.c. of mercuric nitrate, then agitate well and dilute to 57 c.c. mark. The observation is then taken in a 220 m.m. tube, which need not be provided with a vertical tube and thermometer.

The extra 2 c.c. is for the space occupied by albuminous precipitate formed by the lead acetate and mercuric nitrate. The results are calculated as anhydrous sugar in 100 grms. of milk, adopting as before the No. 52.5 as the specific rotation for the D line.

Table showing the Results given by Different Methods of Analysis.

	Fehling, gravimetric	Pavy Fehling, simple dilution.	Pavy Fehling, after separation of casein.	Optical A.	Method B.
1	..	4.45	4.49	4.78	4.69
2	..	4.63	4.71	4.78	4.92
3	..	4.76	4.82	—	5.10

It will be seen that the results are somewhat lower, which I attribute to the more perfect precipitation of the albumenoid, and also to the less error incurred by using 50 grms. of milk without dilution.

It will be seen that there is considerable difference between the methods, the differences between gravimetric and optical method being about 0.30 per cent, whilst there is a fairly close agreement between gravimetric and volumetric method by Pavy Fehling. The latter method is the very rapid one, and accurate if properly carried out. We have not examined the process of Ritthausen by separation of fat and casein by copper sulphate and alkali, believing that it will give no better results than separation by acetic acid and boiling. In the analysis of condensed milks sweetened by cane-sugar it suffices to take the optical activity by the above method, then to take the reducing power and deduct the activity due to lactose, when the remainder is that due to added cane-sugar. Other methods are those of the citric acid inversion process, and lastly, the admirable method of Kjeldahl with invertase.

Tottington, April, 1891.

NEW PROCESS FOR THE ESTIMATION OF SULPHUR IN COAL, &c.

By THOMAS NEILSON.

THE estimation of sulphur in coal and coke is one which is of special importance, not only to the iron and steel works' chemist, but others also, and, therefore, any process which is at once reliable, and at the same time expeditious, will commend itself to all chemists.

With this object in view I will endeavour to give the results of a few of several experiments made in order to test, and make a careful comparison of, a process which I have found to fulfil those conditions of reliance and expedition.

The sample employed was of hard Durham coke, and in each experiment, which was accompanied by a blank one, I used 1 grm. of the sample. Without further premise, I give the results with an explanation below.

	1.	2.	Average.
A. Lime (HCl sol.) . . .	0.76	0.76	0.76
B. Lime (H ₂ O sol.) . . .	0.51	0.53	0.52
C. Magnesia (HCl sol.) . .	0.58	0.58	0.58
D. Magnesia (H ₂ O sol.) . .	0.55	0.52	0.53
E. Fusion (KNO ₃ +Na ₂ CO ₃)	0.51	0.53	0.52
F. Na ₂ CO ₃ +MnCO ₃ . . .	{ 0.76 0.78 }	{ 0.78 0.77 }	0.77

A. 1 grm. of the sample mixed with 2 grms. CaCO₃ and put into a flat platinum dish, and then kept at a low red heat for about one hour, when complete oxidation of sulphur in the coal or coke is accomplished. The platinum dish is then placed in a beaker and covered with water; boil, and add 2 c.c. of bromine water in order to prevent any sulphur escaping complete oxidation; then add 10 c.c. HCl, boil and filter, and precipitate with BaCl₂ in the usual manner.

B. Exactly as in A, except that the digestion is continued for a longer period and then filtered, omitting solution in HCl; then adding 2 c.c. bromine water, acidify with HCl and precipitate with BaCl₂.

C. In the same way as at A, using MgO instead of CaCO₃.

D. In the same way as at B, using MgO instead of CaCO₃.

E. 1 grm. coke fused with 11 grms. KNO₃ and 4.5 grms. Na₂CO₃; then digest in boiling water, adding again 2 c.c. of bromine water, then 20 c.c. of HCl; evaporate to dryness and take up with 5 c.c. HCl and water, and precipitate with BaCl₂.

F. This last process, which so far as I know is an entirely new process, I perform in the following manner:—1 grm. of coke is mixed with 2 grms. of Na₂CO₃ and 0.5 grm. of MnCO₃, and the whole placed in a flat platinum dish and kept at a low red heat (allowing only the bottom to be red) for one hour; after this time all the sulphur and carbon will have been oxidised. The mixture is now fused, then cooled and placed in a beaker with water, or in a basin, and 20 c.c. HCl added; remove platinum dish, and evaporate to dryness and take up with 5 c.c. HCl and water, then filter and precipitate SO₃ in the usual manner. I have found that it is not necessary to evaporate to dryness, but for safety it is advisable. With other samples equally satisfactory results were obtained. It is necessary in this process to make a blank experiment, which should be performed for the same length of time, and, if possible, at the same time when the experiment is made in a muffle furnace.

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NOTE ON THE SOLUTION OF CALCIUM CARBONATE IN CARBONATED WATER.

By Rev. A. IRVING, B.A., D.Sc.,
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SOME little time ago the writer was led to investigate in a general way the evidence which temperature changes might afford as to the existence of a definite chemical compound of the nature of a bicarbonate, when fresh-precipitated CaCO₃ is dissolved in excess of CO₂ in water. For this purpose lime-water of full strength was used. The CO₂ was prepared in the usual way by the reaction of dilute HCl upon lumps of marble; but to prevent the error which might otherwise arise from some of the heat liberated in the reaction being carried over into the lime-water, the very slow current of CO₂ was made to pass first through a column of about 8 inches of distilled cold water. The temperature of this, as indicated by one of Hicks's thermometers, was 10.7° C.

The temperature of the lime-water, which was contained in an ordinary foot-jar, was at the commencement of the passage of the gas 10.2° C. As the CO₂ passed and the CaCO₃ precipitate increased, the temperature gradually rose, heat being evolved by the combination CaO+CO₂=CaCO₃.

The rise of temperature, however, did not cease when the precipitate began to dissolve, the maximum precipitation appearing to be attained in about ten minutes with a temperature 11° C. At the end of twenty-five minutes, the heavy powdery precipitate had well-nigh disappeared, the thermometer immersed in the water in which it had been suspended reading 11.6° C. From this point no further solution appeared to take place, the thermometer reaching 11.7° C. and remaining stationary, while the gas was passed for another 20 minutes. When these facts are plotted out on a diagram along with intermediate temperatures noted, they are seen to form a curve, the gradient of which rises rather rapidly during the precipitation stage, then, as solution sets in, becomes less and less, and finally nil.

It would appear from these results that there is heat evolved (i.) in the precipitation stage, representing the excess of that produced in the reaction CaO+CO₂=CaCO₃ over and above that required for the separation of the water-molecule from the Ca(OH)₂; (ii.) in the solution stage, which we may attribute perhaps to the formation of the hydrogen acid, H₂CO₃, rather than a bicarbonate.

Here another fact of interest was observed. The experiment was continued for about twelve hours the next day, but without completing the solution of the precipitated CaCO₃.

A few days later, CO₂ (washed as above) was passed

through a fresh portion of lime-water for twenty-four hours, and the same failure to effect complete solution was the result. The undissolved portion of the precipitate was filtered off quickly with the aid of an ordinary vacuum arrangement for quick-filtering, and dried (1) in the air, (2) in an air-bath at 50° C. This, on examination with a low power under the microscope, was seen to be distinctly crystallised in the rhombohedral form of Iceland-spar.

A little later a third sample of lime-water was similarly treated, the CO₂ being passed at intervals for several days. On filtering quickly, the following results were obtained:—

- (a) Residue on filter (dried at 120° C.).. = 0.075 grm.
- (b) Residue obtained on evaporating the filtrate down and drying at 120° C... = 0.033 "

The percentages of the whole precipitate deduced from these numbers being (a) 69.4 and (b) 30.6; that is to say, about two-thirds of the precipitate remained undissolved by excess of CO₂ under ordinary atmospheric pressure.

A similar treatment of baryta-water gave very much more surprising results, the percentage of BaCO₃ dissolved in excess of CO₂ being only 8.7.

The arrangement adopted in the above trials was then supplemented by a column of water about 15 inches deep, through which the excess of CO₂ was made to pass, in escaping from the flask (in this case) which held the lime-water acted upon. In this way the whole apparatus became charged with nearly pure CO₂, acting at above a full atmospheric pressure. Under these conditions, the gas being passed intermittently, while the lime-water was in continuous contact with it for a fortnight, the lime-water certainly became somewhat clearer, but nothing like complete transparency was obtained. A like failure to obtain a clear solution resulted from passing a large excess of CO₂, produced by direct combustion of C in oxygen, through lime-water of full strength.

Now when we meet in the text-books with such statements as the following—"If more gas is passed through, the precipitate dissolves," "The white precipitate at first formed gradually disappears, and the liquid again becomes transparent," "If you continue to pass CO₂, the solution finally becomes clear," "When all the precipitate has re-dissolved, the liquid is quite transparent," and so on, those who are engaged in using chemical science as an educational instrument, are surely justified in protesting against such unprecise and therefore misleading and confusing statements.

It is not, however, in the language merely that the want of precision appears to creep in; it shows itself in the rough and inaccurate demonstration, with which many writers of elementary text-books seem to be satisfied. The discrepancy between the actual facts, as stated above, and the statements quoted may arise from one of two causes (leaving out of account the mere compiler who mistakes a paraphrase of passages from another writer for original work): either (1), the lime-water used must have been very poor stuff, or (2) the neglect of washing the CO₂ from the trace of HCl which comes over in a rapid stream of the CO₂ has led to false results. Probably the latter is the more frequent source of error, since in all the experiments described above silver nitrate precipitated AgCl from the wash-water after acidifying with HNO₃.

Slovenliness of statement in text-books and slovenliness of experiment are both calculated to detract from the high educational value of any experimental science. It is the greatest error possible to fancy we can "simplify" by sacrificing accuracy and precision.

Royal Institution.—Dr. E. E. Klein, F.R.S. (Lecturer on Physiology at St. Bartholomew's Hospital), will, on Tuesday next (April 28), begin a course of three lectures on "Bacteria: their Nature and Functions" (the Tyndall Lectures), and Mr. H. Graham Harris, M.Inst.C.E., will, on Saturday (May 9), begin a course of three lectures on "The Artificial Production of Cold."

A QUICK METHOD FOR THE SEPARATION OF CADMIUM FROM COPPER.

By H. N. WARREN, Research Analyst.

THE precipitation of copper as cupric dioxide by means of Fehling's tartrate solution in order to estimate thereby the various sugars, is to all a well-known commercial test, yet few, if any, appear to have adopted this—*vice versa*, thus employing glucose as a reagent in order to estimate copper; the majority of opinions being that the separation of that metal may be only partially complete, or is incomplete unless a certain amount of cupric salt remains in solution. This, however, is without foundation, in so much that the author has succeeded in effecting a complete separation of copper from cadmium by a slight alteration of process.

The alloys under examination have comprised chiefly alloys of zinc, copper, cadmium; the alloy being brought into solution by the aid of nitric acid, diluted to 100 c.c., and a convenient quantity withdrawn, corresponding to an equivalent in grms. taken. The solution is now diluted and an excess of Rochelle salt added, together with a sufficiency of sodic hydrate. The whole is then heated to boiling, which should appear perfectly clear and free from any precipitate. To the boiling solution is now added, in quantities of not more than 4 c.c. at a time, a dilute solution of glucose, the solution being further boiled upon each addition. The cuprous oxide which is thus precipitated should possess a pure scarlet tint, is filtered, washed free from impurities, and decomposed by ignition in a porcelain crucible, cooling, and re-igniting with a few drops of strong HNO₃, weighing the so treated precipitate as CuO.

The filtrate, which now contains the whole of the cadmium and zinc, is acidified and warmed, a current of SH₂ being passed through the same until saturated; the precipitated cadmium sulphide thus formed being collected, washed, and dissolved in a small quantity of HNO₃, being afterwards re-precipitated as carbonate by the addition of sodic carbonate.

The second filtrate, containing the zinc, is again rendered alkaline and precipitated as zinc sulphide by the addition of ammonium sulphide, the precipitate dissolved in HCl, and re-precipitated as in the former instance. With slight precautions, perfectly reliable estimations may be thus brought about; the copper being so completely separated as to produce no colouration upon the addition of a solution of K₄FeCy₆ to the zinc and cadmium filtrate.

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MORDANTS IN DYEING AND THE THEORY OF MENDELEEFF.

By M. PRUD'HOMME.

THE mordants employed for fixing colouring matters upon vegetable fibres are metallic oxides, such as those of aluminium, chromium, iron, and tin, to mention those only which are in the most general use. The oxides intimately combined with the fibre retain or attract the colouring matter, with which they form lakes of different tones. For instance, with alizarin and the oxides of the above metals we obtain red, garnet, violet, and orange.

When studying from this point of view the oxides and their reciprocal influence in mixtures, the author succeeded in detecting relations between the shades obtained as functions of their atomic weights. More precisely these shades undergo continuous variations, which are very distinct if we adopt Mendeleeff's classification of the elements in natural groups and periodic series.

The principal bodies studied are:—Li, B, Na, Mg, Al, Si, P, Cl, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Z, As, Br, Sr, Mo, Ag, Cd, Sn, Sb, I, Ba, Di, Ce, La, W, Hg, Pb, Bi, U.

He has not been able to study Be, Ga, Ti, In, and Tl for want of material.

The results of numerous experiments made under the most varied conditions may thus be formulated:—

1. In each of Mendeleef's groups, if we consider the terms of the periods of the even or odd rank, there is a continuous variation in a determined direction from blue to red, or from red to blue. This is the phenomenon presented respectively by Mg, Zn, Cd, and by Ca, Sr, Ba.

It has been found that for the triplets, such as Mg, Zn, Cd—Ca, Sr, Ba—K, Pb, Cs, the increase of the wave length of the corresponding rays is proportional to the increase of the atomic weight. The metallic oxides have therefore the property of communicating to their combinations with colouring matters luminous vibrations related to those of their metals.

2. In each period from the first to the fourth group, there is a progression towards the red. From the fifth to the eighth there is a movement from red towards blue.

This law is easily verified for the periods 3, 5, and 11.

3. The Group IV. does not represent a maximum, properly speaking, as the shades corresponding to it (in the periods of the odd rank) contain an excess of yellow.

With alizarin Sn gives a decided orange, Cd and Sb reds, Pb a reddish orange, Hg and Bi shades much more red.

In the 4th period the orange term does not belong to the Group IV., but recedes to Group V., where it is represented by vanadium with a distinctness which is emphasized by the vicinity of chrome, manganese, and iron, the compounds of which with alizarin are respectively garnet-red, violet-red, and violet. This period IV., like the 6th and the 10th, contains more terms than the others, and it is not surprising that the orange element is transferred more towards the right of the table.

Tin, the central term of the system, with an atomic weight 118, equal approximately to half that of uranium (240), ought to be, and is in fact, the especial representative of the yellow and orange tones. This is a fact which the practice of dyeing has established long ago.

The author remarks that the sulphides of Cd, Zn, Sn, Sb, Te (bodies belonging to the 7th period) are all yellow or orange.

Besides the method of producing shades on the fibre we may employ that of lakes, which consists in precipitating the oxides from their saline solutions by means of an alkali or an alkaline salt (borate, silicate, phosphate) in presence of a soluble colouring matter, such as alizarin or alizarin blue, &c. There is often between the results obtained upon the fibre and those of which the lakes are the manifestation a total inversion, i.e., the bluest term becomes the reddest, and inversely.

The alizarin violets with iron, on the addition of Mg, Zn, Cd, vary from red to blue; but with Ca, Sr, Ba, from a blue to a red.

Solutions of the salts of Mg, Zn, Cd, to which is added an ammoniacal solution of alizarin, yield a blue lake for Mg, a yellowish red for Zn, and a violet for Cd. With solutions of the salts of Ca, Sr, Ba the reddish lake is that of Ca, and the most blue that of Ba.

The influence of bases is shown by the mere presence of their salts: solutions of the sulphates of Li, Na, and K yield, with an ammoniacal solution of alizarin, shades passing from violet to red. We may admit that the base of the salt is divided between the acid and the alizarin—a body having an acid function. The influence of the bases is not less decisive.

It is not the same with that of the acids, though it seems that differences may be shown between the shades of the solutions of KCl, KBr, and KI.

The action of Cl, Br, and I (analogues of Mg, Zn, Cd) is distinctly felt in the series of colouring-matters derived

from fluoresceine (eosine, primerose, Magdala red, &c.). These are tetrachlorides, tetrabromides, and tetraiodides of fluoresceine or bodies containing at once Cl and Br, Cl and I, Br and I. Their tones differ decidedly. In this case the fluoresceine nucleus may be considered as the mordant, and Cl, Br, I as the colouring matter.

The author does not pass in review each group or each period. He observes that in the groups the law of progression continues itself to the last term. P, As, Sb, Bi accentuate the passage from blue to red. In the Group VI. it is the same. Cr gives with alizarin a garnet red, which is transformed in passing by Mo and W, and changes at last with U into a violet, the bluest obtained with a single oxide.—*Comptes Rendus*, cxii., p. 236.

ON A NEW METHOD OF SEPARATING IRON FROM COBALT AND NICKEL.

By G. A. LE ROY.

It is known that one of the best methods for the determination of cobalt or nickel consists in electrolyzing the solution of these metals, which may be alkaline or neutral, or even slightly acid.

It is known that in this electrolytic determination, manganese, mixed with cobalt or nickel, does not interfere, since it is deposited at the positive pole in the form of a hydrated peroxide without carrying cobalt down with it. It is not the same with iron, which must first be separated by one of the ordinary methods of precipitation. But the methods for the separation of iron from cobalt or nickel are long and tedious, as the process has to be repeated several times.

The author has sought for a method which will permit of the separation of iron by the galvanic current.

The metals cobalt or nickel, manganese and iron (in the maximum degree of oxidation) must be in a sulphuric solution. To the liquid is added a quantity, as small as possible, of a non-volatile organic acid (by preference the citric). There is then added a large excess of a strong solution of ammonium sulphate rendered very decidedly ammoniacal. Under these conditions, ferric oxide is not precipitated in presence of citric acid.

Into the ammoniacal solution of the metallic sulphates there are introduced the platinum electrodes of any electrolytic apparatus. The current of two Bunsen or Poggendorff elements (= 300 c.c. of detonating gas per hour) is then allowed to act. The manganese is deposited at the + pole, the nickel or cobalt is deposited along with the iron at the — pole.

After the deposition of the metals is completed, the current is interrupted. The negative electrode is removed, washed rapidly with boiling distilled water, and placed in a concentrated solution of pure ammonium sulphate supersaturated with caustic ammonia, and it is then connected with the + pole of the battery. Into the ammoniacal solution there is then introduced a second platinum electrode, previously tared, which is then connected with the — pole. The current is then again allowed to act (= 100 c.c. of detonating gas per hour). The electrode, on which the Co, Ni, and Fe are deposited, takes the part of the solvent electrode; the metals are oxidised by the influence of the current; but, whilst the cobalt and nickel dissolve in the ammoniacal liquor and are deposited in the metallic state on the negative electrode, the iron, transformed into ferric hydroxide, insoluble in the ammoniacal liquid, remains partly on the negative electrode and floats partly on the solution. The precipitate of ferric hydroxide formed under these conditions does not carry down with it any appreciable traces of cobalt or nickel, and these metals are entirely deposited at the negative pole.—*Comptes Rendus*, cxii., p. 722.

SEPARATION OF TIN AND TITANIUM.

By H. HAAS.

THE author, in an Inaugural Dissertation, proposes a new method founded on the well-known fact that tin oxide is reduced to metal by ignition in a current of hydrogen, whilst this is not the case with titanitic acid. The latter, indeed, is reduced partially or entirely to a lower stage of oxidation, for the white or yellow colour of the titanitic acid is converted into a grey verging upon violet; but this lower stage of oxidation is again converted into titanitic acid on boiling in dilute hydrochloric acid.

After both oxides have been ignited in a current of hydrogen the metallic tin is dissolved by treatment with hydrochloric acid in heat, and the tin is thrown down from this solution by means of sulphuretted hydrogen after the excess of acid has been partially neutralised.

In the insoluble residue the titanitic acid is determined by Lévy's process. The residue is fused with potassium bisulphate, the melt is taken up in water, acidifying the solution if necessary, and the liquid is neutralised with potassa or ammonia. After 0.5 per cent of the volume of undiluted sulphuric acid has been added it is boiled for six hours to precipitate the titanitic acid, adding more water to compensate for the loss of oxidation. This method is not applicable in presence of ferric salts.

In their absence, according to the experiments of Haas, it gives satisfactory results. The solution of the melt with potassium bisulphate requires much time; hence the author prefers to melt with potassium carbonate, which admits more rapidly of a clear and complete solution of the melt, if instead of dilute sulphuric acid the undiluted acid is cautiously and gradually added.

In the separation of tin oxide and titanitic acid the author proceeds as follows:—

As the reduction of tin oxide in a Rose's crucible or in a porcelain boat is but incomplete, the mixture of tin oxide and titanitic acid is placed directly in a dry tube of the most infusible glass, and ignited for about fifteen minutes in a current of hydrogen over a common Bunsen burner. After being allowed to cool thoroughly in a current of hydrogen the grey mass is rinsed with water into a beaker, and if a small portion adheres to the side of the tube it is dissolved away by touching with dilute hydrochloric acid, and subsequent rinsing with water. About 30 c.c. of hydrochloric acid at 20 per cent are then added, and the liquid is kept for half an hour at a gentle boil. When cold it is filtered, and the residue is washed with hot water.

The filtrate is neutralised, slightly acidified, and treated with a current of sulphuretted hydrogen. After standing for some time in a warm place the precipitated tin sulphide is collected on a filter, washed with water, to which a little ammonium acetate has been added, and dried. After the precipitate has been cautiously separated from the filter and the latter incinerated, the tin sulphide and the ash of the filter are again reduced by gentle ignition in a glass tube in a current of hydrogen.

The reduced tin is washed with water and a little dilute nitric acid into a capacious porcelain crucible, mixed with about 10 c.c. dilute nitric acid; evaporated to dryness on the water-bath; the residue is again taken up with nitric acid and hot water, and the tin oxide is determined in the ordinary manner.

According to the author, the washed and dried tin sulphide may also be easily determined by igniting the precipitate along with the ash of the filter in a weighed reduction tube in a current of hydrogen and weighing it as metal. It is less advisable, especially if the quantity is large, to use asbestos filters, and to reduce the tin sulphide collected upon these, as the filtration is exceedingly tedious.

In treating the residue of the reduced mass (titanitic acid) with hydrochloric acid it is burnt along with the filter and melted in a platinum crucible with 10 parts of

potassium carbonate. The melt is moistened with about 200 c.c. of water and concentrated sulphuric acid drop by drop until the acid potassium titanate dissolves. The clear or perhaps slightly opalescent solution is neutralised with sodium carbonate, 2 grms. of concentrated sulphuric acid are added, the solution is made up to 400 c.c. with water, and boiled for six hours, replacing the water as it evaporates. On account of the unavoidable "bumping" it is boiled in a capacious well-glazed porcelain pan, which may be conveniently covered with a large clock-glass or an inverted funnel.

After the titanitic acid which separates out has been filtered off and washed with hot water, the filtrate is measured, mixed with so much concentrated sulphuric acid that the liquid may contain $\frac{1}{4}$ per cent concentrated sulphuric acid, and again heated to a boil; a separation rarely takes place. The titanitic acid collected upon the filter is weighed as such after drying and ignition.

The results communicated by the author show that the separation of tin and titanium can be accurately effected in this manner:—

To make the method applicable in the case of ores containing silicates the silica must first be removed, which is readily effected by evaporating down with hydrofluoric acid, when tin and titanium remain in the residue.

The separation of iron from titanitic acid is less easy. As already mentioned, ferric salts must not be present in Lévy's method. The proposal to prevent the precipitation of the iron when separating the titanitic acid (by reducing the ferric salt to the ferrous state) does not always succeed. Haas, therefore, proceeds as follows:—

Titanic acid in presence of a ferric salt is separated exactly according to Lévy's instructions. The separated ferrihydrous titanitic acid is filtered off, ignited in a glass tube in a current of hydrogen, which is kept up until the product is cold. The reduced grey mass is then rinsed into a small beaker, boiled for half an hour with hydrochloric acid at 20 per cent; the white residue is collected upon a filter, washed, and weighed as pure titanitic acid.

In determining tin and titanium in a mineral, 5 to 10 grms. of the substance, finely ground and sifted, are placed in a platinum capsule or a roopty platinum capsule upon the water-bath, and opened up with dilute sulphuric acid (1:10) and hydrofluoric acid, so that the silica is completely volatilised, and the residual compounds are converted into sulphates. The absence of hydrofluoric acid is ascertained by a further addition of sulphuric acid, evaporation on the water-bath, and heating the residue over the open flame. Neither hydrofluoric nor silicic acid must be present in the residue. Water is then added, the whole is heated for some time, and the contents of the vessel in which the sample was opened up (without filtering off the residues) are rinsed into a spacious porcelain pan, and, as indicated above, boiled in presence of $\frac{1}{4}$ per cent of concentrated sulphuric acid for six hours after dilution to 400 c.c. It is then cooled, filtered, washed out with hot water, examining if a further deposit is produced in the filtrate on boiling again in presence of $\frac{1}{4}$ per cent sulphuric acid. If a precipitate appears it is collected like the former. The precipitates, which contain all the tin and the titanium, are placed in a porcelain crucible, the filters are burnt cautiously, the whole ignited gently for some time with access of air; the contents of the crucible are rinsed upon a filter, and washed with hot water.

After the residue has been dried and again gently ignited in a porcelain crucible, it is placed in a dry tube of sparingly soluble glass, and ignited in a current of hydrogen for a quarter to half hour.

The reduced mass is then, as above directed, treated with hydrochloric acid; the undissolved residue is again submitted to reduction and treated as before. The tin is determined in the combined filtrates in the manner above described.

The residue left after the second treatment with hydrochloric acid is fused in a platinum crucible with 6 to 10

parts of potassium carbonate until everything is dissolved, subject first published by the Elisha Mitchell Scientific Society, and afterwards by the CHEMICAL NEWS and the *Journal of Analytical Chemistry* (vol. iii., p. 48). This seems to have been the first article published in the discussion, but to Dr. Brauner, of Prague, belongs the credit of arousing the discussion which was carried on in the *Berichte* of the German Chemical Society during 1889, and which was participated in by Ostwald, Meyer and Seubert, and Brauner.* Meyer and Seubert alone opposed the adoption of $O=16$ as the standard.

If the titanous acid seems to contain a trace of iron it is again reduced in a current of hydrogen, and the iron is dissolved out with hydrochloric acid.—*Zeitschrift f. Anal. Chem.*

THE PROPER STANDARD FOR THE ATOMIC WEIGHTS.*

By F. P. VENABLE.

AMONG the important questions attracting the attention of chemists to-day is that of the proper standard to be adopted for the atomic weights. It is a question whose settlement cannot be much longer postponed without injury. It must be settled by careful consideration on the part of associations and individuals, and then by general usage—a sort of majority vote. I therefore venture to bring the question in its present status to the attention of this body of chemists, asking a careful, thoughtful discussion and consideration of it.

Two elements lay claim to the position of standard for all other atomic weights, hydrogen and oxygen. Hydrogen is called by Meyer and Seubert the Dalton-Gmelin unit, and oxygen the Wollaston-Berzelius unit. The contention is an old one then, and first one then the other has been forced to give way in the struggle. For a long time oxygen was the accepted standard of the only approximately accurate atomic weights—those of Berzelius. It was then displaced by hydrogen, and this element has so fixed itself in the literature that it cannot well be in turn displaced as the unit. But I would make a careful distinction between unit and standard. To make a radical change now would be inconvenient and difficult, and should be done only under stress of absolute need. When one considers the difficulty and tediousness of becoming accustomed to new numbers, and the decrease in value and intelligibility of all the literature in the old notation that would follow a change of unit, one can properly realise the cost of such a change.

We are closing a century's labour, however, and a century's history, and it is important that we should come to some agreement on this point, and so be in a position to confer some degree of constancy upon our so-called constants. As it stands now, each revision or re-determination is calculated by two standards, and the individual chemist is left to choose between them at his own sweet will. There is no necessity for this, and it is a blot upon our science. Other sciences, notably electricity, are getting their standards in order, their loins girt, as it were, for the race of the twentieth century. We must settle this question, as well as others, if we would move freely in the grand onward march.

The best settlement comes, as is so often the case, in the way of a kind of compromise. Let oxygen be the standard, and hydrogen practically the unit. This reduces the changes to the least possible, and tables arranged on this basis have been in use a long time. In fact, it was only with the idea of securing greater accuracy that this arrangement was ever changed. The use of $O=15.96$ as a factor for calculation appeared about the time of the first appearance of Meyer's work on the "Modern Theories of Chemistry," and is mainly due to his instrumentality. The pursuit of accuracy in that direction has proved an *ignis fatuus*, and the necessity for something more fixed becomes every day more and more apparent.

The extent of this need impressed me greatly while studying the various re-calculations of the atomic weights as made by our own Prof. Clarke, Meyer and Seubert, Sebelien and Ostwald, and lead to an article on the

first published by the Elisha Mitchell Scientific Society, and afterwards by the CHEMICAL NEWS and the *Journal of Analytical Chemistry* (vol. iii., p. 48). This seems to have been the first article published in the discussion, but to Dr. Brauner, of Prague, belongs the credit of arousing the discussion which was carried on in the *Berichte* of the German Chemical Society during 1889, and which was participated in by Ostwald, Meyer and Seubert, and Brauner.* Meyer and Seubert alone opposed the adoption of $O=16$ as the standard.

Without dwelling separately on these articles, or the arguments adduced on one side and the other, I shall content myself with trying to state clearly the reasons for adopting $O=16$ as the standard. Were it a mere matter of sentiment, of securing a larger number of integers in the table of atomic weights, or something of that kind, I think all will agree with me that the change would be mere folly. Such men as Ostwald and Brauner would not waste time quibbling over anything so insignificant. There must be and is something deeper, and it is strange to me that Meyer and Seubert seem unable to see the true point of contention.

The facts of the case are as follows:—Hydrogen, as having the least atomic weight, seems at first sight the most appropriate unit for measuring the others. It admits of all being represented by numbers greater than unity, and none of them of such inconvenient size as in the Berzelius table with $O=100$. If we could determine the ratio of the other elements to hydrogen directly, that is, if their atomic weights were determined by means of hydrogen, and hence were directly dependent upon this as unit, there would be nothing further for us to desire. Unfortunately, very few such direct ratios can be secured. Only three or four have been determined.

Under these circumstances, two things are possible. First find the ratio between hydrogen and oxygen, then, using this as a factor, calculate the other atomic weights. Could we find this ratio absolutely, there would be no objection to this method, but it is impossible to eliminate or allow for personal and experimental errors. The ratio found can at best be but an approximation. Evidently, by using an approximation to calculate other approximations, we get further and further from the truth. As Ostwald has said, we are introducing totally uncalled for and unnecessary errors, and he is right in styling it, in this stage of our science, a barbarism. As Brauner has pointed out, these errors can easily amount to several integers, in the higher atomic weights.

It is not for lack of skilled workers to undertake the determination of this ratio. Much excellent work has been done upon it, and especially in the last two or three years. Ostwald has summed these up, and says there is an error of at least 0.3 per cent which has not been removed by recent workers. Brauner agrees with him that the variations are irreconcilable, and though Meyer and Seubert think the ratio can vary but little from that assumed by them as justifiable by the best determination, it is manifestly a point on which the best authorities differ and hence one of uncertainty.

Why should we then make use of the number 15.96 if it is not fixed by incontrovertible, unerring, universally accepted experiments? It makes the matter no whit better for Meyer and Seubert to profess their willingness to re-calculate their table should a change in the number 15.96 prove necessary. It is merely a confession of the insecurity of their own position. We do not wish any re-calculation. We wish a standard by which the calculations can be made once and for all, one that will give us the least possible error, and is itself independent of other calculations. The present use of the double stan-

* See *Chem. Zeit.* 1890, No. 13, where Dittmar says: "Ich wage zu hoffen, dass diejenigen Chemiker, welche seither, nachdem sie die Ueberzeugung gewonnen hatten das $O: H$ kleiner ist als 16, darauf bestanden haben, dass $H=x$ als Einheit für die Atomgewichte festgehalten werden müsse, diese absurde Praxis aufgeben und den 16 Theil des Atomgewichtes des Sauerstoffs als Einheit adoptiren werden."

* A Paper read before the American Association for the Advancement of Science.

dard 15.96 and 16 seems puerile and leads to all manner of inaccuracies.

The second possibility is to use oxygen as the standard.

The question reduces itself, then, really to this:—Shall we use $O=15.96$, or $O=16$? For oxygen must be used from very necessity. If $O=15.96$ is not the absolute ratio or is not generally accepted as such then the reason for its use ceases.

It is not necessary to bring forward arguments as to the relative convenience of the two, nor as to their effect upon the periodic law. Such arguments have little weight or significance when it is seen that the question lies between $O=15.96$ and $O=16$, and that hydrogen can never be the actual standard or factor from purely chemical reasons. Nor yet is there much in any argument from analogy with other standards and units. Such only lead us away from the one all-important consideration—the avoidance of unnecessary errors.

I have said that the present proposition could be looked upon in the light of a compromise. If oxygen takes the place of hydrogen as standard, what falls to the share of the latter element? If oxygen were made 100, as in the Berzelius table, or 10 or 1, as have been proposed, then the present numbers, as referred to hydrogen, would be entirely changed and lost sight of. The plan is to change them as little as possible, giving oxygen the number 16, which was once regarded as the ratio between it and hydrogen, and, according to the views of some, may still be it. Then the number for hydrogen will vary very little from unity, and the whole table is nearly based upon it as the unit. This number will change from time to time with new determinations, but such changes will involve no others. Oxygen, the standard, will then be fixed, and our task lies in the accurate determination of the others by it.

Meyer and Seubert cling to the idea that if oxygen be adopted it must be taken equal to unity, maintaining that $O=16$ is neither flesh nor fowl, and by no means a unit. It is true that the standard or basis of a series of physical constants has in the past usually been taken equal to unity, but I cannot conceive the power of this habit to be sufficiently strong to force us into inconveniences or inaccuracies. That it is not regarded as a binding rule has been shown by the choice of some recent standards, especially in the new science of electricity.

The atomic weights are but relative numbers. To be in any respect constants, they must be relative to but one single element. With but few exceptions, the ratio to oxygen can be determined. In revision of atomic weights, then, this should receive the chief attention, and the oxygen ratio should be most carefully and directly determined.

Where the intermediation of another element is made use of (even though this be one which "may be counted among those of which the atomic weights are already known with the nearest approach to exactness," as Dr. Mallet recommends), it must be borne in mind that the result is subject to a certain error, which is generally multiplied several times and hence cannot give concordant results with the direct oxygen ratio, and less stress must be placed upon it. If the well-determined ratio $H:O$ is subject to an error of 0.3 per cent, how much greater is the error in the case of ratios less well known?—*Journal of Analytical Chemistry*.

The Methods for Determining the Melting Points of Organic Substances.—H. Landolt (*Berlin Akad.*).—The following methods were tested:—1. Fusion and congelation of large quantities of the substance in which a thermometer is plunged. 2. Heating the substance in capillary tubes of different forms. 3. The electric method.

ON THE
ATOMIC WEIGHT OF OXYGEN.*

By E. H. KEISER.

IN a recent paper† on this subject, Mr. W. A. Noyes makes a statement which is not in accordance with the facts, and which, as it may be misleading to some, deserves to be corrected. Mr. Noyes states that he has pointed out a source of error in my determinations of the atomic weight of oxygen. I desire to call attention to the fact that Mr. Noyes has merely pointed out what he supposes to be a source of error in my determinations, which is quite different from having pointed out a source of error. Moreover, Mr. Noyes' supposition is not well founded, and is not in accordance with the results of experiments.

The point in question is this:—It was found as the result of direct experiments that the hydrogen which was driven out of the palladium tube contained a trace of moisture; this moisture was collected in a phosphorus pentoxide tube, and its weight was subtracted from the apparent weight of hydrogen. Mr. Noyes thinks that there could not have been moisture present in the hydrogen, and that the increase in weight of the pentoxide tube should not have been deducted from the apparent weight of hydrogen. But I had found by direct experiment that moisture was present, and was, therefore, obliged to insert a weighed phosphorus pentoxide tube. Mr. Noyes thinks that the moisture came from the gases that were subsequently passed through the tube, but, as I have clearly stated in my paper, these gases were thoroughly dried by passing through concentrated sulphuric acid and over phosphorus pentoxide before entering the tube in question, so that this supposition is also without foundation.

The fact remains that the atomic weight of oxygen as determined by the combustion of weighed amounts of hydrogen, the hydrogen being obtained from palladium hydrogen, is 15.95, and not a lower value, as Mr. Noyes thinks he has shown it to be. Nor can I agree with his statement that it is almost certain that the true atomic weight of oxygen is not greater than 15.90. Before coming to such a conclusion, it is well to remember that all recent determinations of this atomic weight, like the older ones of Dumas, and Erdmann, and Marchand, have been determinations of the composition of water by difference, that is, only two of the three quantities have been determined directly. In all the determinations it is assumed that the hydrogen or oxygen which is weighed is really all present in the weighed quantity of water, or, that the hydrogen and oxygen which have been weighed have combined completely with one another. In other words, no complete syntheses of water have yet been recorded. The words *complete syntheses* are here used in the sense in which they were used by Stas in his researches on the atomic weights of silver, chlorine, &c. To make a complete synthesis of water it is necessary to weigh separately the hydrogen, the oxygen, and the water formed by the union of the weighed amounts of hydrogen and oxygen. It seems to me that it is too early to come to any conclusion as to the true value of the relation between hydrogen and oxygen until this relation shall have been determined by the complete gravimetric synthesis of water.

I have recently made determinations of the atomic weight of oxygen by a method which permits of the separate weighing of the hydrogen, the oxygen, and the water. In brief, the method is as follows:—A glass vessel containing spongy palladium and provided with a three-way stop-cock is exhausted with an air-pump, and as perfect a vacuum obtained as is possible with a mercury-

* From the *American Chemical Journal*, Vol. xiii., No. 4.

† *Journal of Analytical and Applied Chemistry*, v., 36; *Ber. d. Chem. Ges.*, xxiv., 238.

pump, and the weight of the empty vessel determined. Pure hydrogen from hot palladium is passed over phosphorus pentoxide and into the exhausted vessel. After the spongy palladium is saturated with the gas, the vessel is again exhausted, and the increase in weight after again weighing is the weight of hydrogen occluded. Pure oxygen is now admitted to the palladium hydrogen until present in excess; the hydrogen is completely converted into water at low temperatures. The weight of oxygen admitted is determined by again weighing the vessel. Now a weighed phosphorus pentoxide U-tube is attached to the palladium vessel, and the excess of oxygen, together with any nitrogen if it was present in the oxygen, is removed by the air-pump. The loss in weight of the palladium vessel and the pentoxide tube (both weighed together) gives the excess of oxygen. The water is thereupon completely transferred from the palladium to the pentoxide tube, and the increase in weight of the latter gives the weight of water formed. The weights of the hydrogen, oxygen, and water are thus determined separately and by direct weighings. Two weighings are involved in the determination of the hydrogen, two weighings also give the weight of water, and from three weighings the weight of oxygen is obtained. Thus far I have made three determinations, and in each one the sum of the weights of hydrogen and oxygen agrees with the weight of water found to within 0.2 of a milligram, and the weight of the palladium tube at the end of the determination was found to be the same as at the beginning. The three results agree quite closely with one another, and give for the atomic weight of oxygen almost exactly the whole number, 16. After a larger number of determinations have been made, I shall publish the details of the method and of each separate determination.

I shall not here enter into a critical discussion of the method used by Mr. Noyes. It might lead to a controversy and a waste of time. It would, however, not be difficult for any thoughtful reader of his paper to see where inaccuracies might perhaps have crept into the work, and several sources of error have already been shown by Mr. G. S. Johnson (*CHEM. NEWS*, lix., 272) to exist in the method, which, it seems to me, have not been completely disproved by Mr. Noyes. Nor is it possible to regard the use of sticks of caustic potash for the purification of hydrogen as unobjectionable. The sticks, as Mr. Noyes states, gradually dissolved in the water carried over. But sticks of potash contain air, and when they dissolve the air is set free, and thus the hydrogen is rendered impure.

THE ELECTROLYSIS OF THE METALLIC SULPHOCYANIDES.*

By LEE K. FRANKEL.

In a paper published by Dr. Smith and the author, in the *Franklin Institute Journal* for August, 1889, the statement is made that manganese, when deposited from a solution containing an excess of potassium sulphocyanide, separates as a greyish white compact deposit on the negative pole, differing in this respect from solutions of the nitrate or the sulphate, from which manganese is deposited as oxide. Furthermore, it is stated that nickel, cobalt, iron, and several other metals separate very rapidly from cold sulphocyanide solutions under the influence of a weak current. In the following paper, the above experiments have been repeated, and the action of the current has been tried on various other metallic sulphocyanides. The results obtained have been, for the most part, of a negative order, but are here appended, as they illustrate some new facts in electro-chemical analysis.

Decomposition of Alkaline Sulphocyanides.—If a concentrated aqueous solution of potassium or ammonium sulphocyanides (300 grms. in 1 litre) is subjected to the action of a weak current (1.5 c.c. OH gas per minute), the solution at first remains clear. After from one to two hours it gradually becomes turbid, and an odour of hydrocyanic acid is readily perceptible. If the current is allowed to run for twelve hours, the turbidity constantly increases until at length the solution is filled with a lemon-yellow amorphous deposit. According to Bunge (*Ber.*, iii., 297), who investigated the action of the current on potassium sulphocyanide, and to Lidow (*Ber.*, xvii., ref. 252), who obtained similar results with ammonium sulphocyanide, this yellow deposit is pseudosulphocyanogen.

If, however, the solution, while being electrolysed, is heated on a water-bath, there is evolved along with the pseudosulphocyanogen an unbearable sickening odour, due in all probability to the formation of organic sulphur compounds. In dilute sulphocyanide solutions, however, the formation of the lemon-yellow compound takes place in but small quantities, and only after the lapse of considerable time, so that if the current be sufficiently weak and the solution sufficiently dilute, no turbidity whatever occurs in the solution. It was anticipated that this behaviour of the dilute solution could be utilised for the electrolytic deposition of the metals, but the other products of decomposition exerted such an influence on the solution that in but very few cases were quantitative results obtained. These are given below as they were found.

Mercury.—Mercury can be completely deposited from solutions of potassium or ammonium sulphocyanide. The metal separates very rapidly from the respective solutions, and resembles the deposit obtained in the electrolysis of the double cyanide of mercury and potassium, in that it never possesses a drop-like appearance, but is dense and coherent.

In the first determination a slight turbidity occurred, due to the larger quantity of ammonium sulphocyanide. The filtrates from all the four determinations gave the blood-red colour with ferric chloride, but did not darken on the addition of ammonium sulphide. The deposits were washed, first with cold, then with hot water, and eventually dried on the edge of a warm iron plate.

	Mercury present. Grm.	Ammonium sulphocyanide. Grms.	Time. Hours.	Current. OH gas per minute. C.c.	Dilution.	Mercury found. Grm.
1.	0.2292	1.5	16	1	75	0.2289
2.	0.2292	0.9	16	1.4	75	0.2285
3.	0.2292	0.9	16	0.65	75	0.2295
4.	0.2292	1.2	16	0.65	75	0.2294

Gold.—Like mercury, gold can be completely deposited from a solution of ammonium sulphocyanide. The metal separates as a compact firmly-adherent deposit, which can readily be washed with either hot or cold water. The conditions under which the deposits were obtained are as follows:—

1. To a solution of gold chloride containing 0.0185 grm. of gold, 1.5 grms. of ammonium sulphocyanide were added, along with 150 of water. A current of 1 c.c. OH gas per minute was allowed to act for six hours, at the end of which time the metal was completely deposited. The gold found weighed 0.0183 grm.

2. The conditions in this determination were like the above, excepting that the gold chloride solution contained 0.1443 grm. of gold, and that the current was allowed to act for sixteen hours. The resultant gold weighed 0.1439 grm.

Cadmium.—If ammonium sulphocyanide is added to a solution of cadmium sulphate, the solution remains clear. If this solution be now subjected to the action of the current, the cadmium immediately deposits as metal, but in a very spongy form. This sponginess is frequently of such an extent that the deposit spreads in a continuous layer

* Read at the Meeting of the Chemical Section of the Franklin Institute, January 20, 1897.

from the negative to the positive pole, and readily detaches itself when washed. Various conditions of current and solution were tried in order to remedy this result, the current used varying from 0.25 c.c. to 2.2 c.c. OH gas per minute, and the amount of ammonium sulphocyanide from 0.3 grm. to 6 grms. in solutions diluted from 50 to 200 c.c. In all cases, however, the cadmium deposited in a spongy form, and the method had to be abandoned.

Palladium, Nickel, Cobalt, and Zinc.—In the electrolysis of neutral solutions of these four metals in the presence of ammonium sulphocyanide, similar reactions took place. In each instance, the metal began to deposit immediately with currents ranging from 1 to 2 c.c. OH gas per minute, in solutions averaging 1 grm. of ammonium sulphocyanide. In the case of the nickel and the cobalt, the metals deposited in a compact metallic form, and frequently could be separated as a thin film from the sides of the platinum dish. With all four metals, however, the deposition continued only to a certain point, after which a reverse action took place, and the coatings gradually dissolved. In the case of the zinc, after permitting the current to act for twenty-four hours, every portion of the grey metallic deposit obtained in the earlier stage of the operation had gone into solution. The probable cause for this singular action lies in the fact that in the decomposition of the alkaline sulphocyanides there is formed an estimable amount of alkaline cyanide which, in the experiments above referred to, could be easily recognised by its odour. The addition of ammonia to the solution from time to time during the passing of the current gave no beneficial results, and all attempts to deposit the metals completely, with the strength of current used, proved futile.

Iron and Manganese.—The continuation of the investigation, previously reported, on these metals led to no satisfactory results. As has been stated, the metals can be deposited from solutions of their sulphocyanides, but not completely, and the tendency to oxidise is so great that films of the oxides form on the edges of the solutions, even during the action of the current. As soon as the solutions are poured off, and the surfaces of the metals are exposed to the air, these films of oxide rapidly spread over the entire deposits, and exclude any possibility of the estimation of iron or manganese by this method.

Arsenic.—Varying quantities of ammonium sulphocyanide were added to solutions of sodium arsenate and of sodium arsenite made alkaline with sodium hydrate. In no case was there the faintest deposition of metal.

Lead.—It has already been shown that when a solution of lead nitrate is subjected to the action of the electric current, the lead will deposit as peroxide on the positive pole. If, now, ammonium sulphocyanide be added to the solution, while the current is passing the lead will deposit itself similarly to the manganese, in that the peroxide of lead gradually dissolves off the anode, while the metal deposits on the cathode. This deposition of metal will continue until no more lead can be detected in the filtrate, but, while the greater portion of the lead has separated as metal on the negative pole, a white coating will now be found on the positive pole, which after solution in acids gives a reaction with hydrogen sulphide for lead. This coating on the anode prevents any quantitative estimation of lead in an ammonium sulphocyanide solution. The metal as deposited from such a solution has a grey metallic appearance, is but loosely adherent to the dish, and easily becomes covered with a yellow film of oxide.

Antimony, Bismuth, and Tin.—To the hydrochloric acid solutions of these metals, ammonia was added until precipitates formed; varying quantities of ammonium sulphocyanide were then added to the respective solutions, followed by hydrochloric acid, until the precipitates just dissolved. All three metals deposit rapidly from such solutions, the tin, however, but incompletely. The filtrate from the bismuth gave no reaction for the metal, but the deposit was so spongy that it could not be handled. The antimony deposit detached itself so readily from the sides

of the dish on which it separated that no effort was made to discover if quantitative results could be obtained.

Pseudosulphocyanogen.—In a paper on the preparation of a new yellow dye colour, H. O. Miller (*Ber.*, xviii., ref. 676) states that the impure compounds, which he designates "Kananin," is obtained by the action of hydrochloric acid and potassium chlorate on potassium sulphocyanide. The resulting yellow substance dissolves in potassium hydrate solution, from which alcohol deposits the potassium salt. If the latter is filtered off and dissolved in water, hydrochloric acid re-precipitates the dye-stuff. As noted above, Lidow (*Ber.*, xvii., ref. 252) asserts that the yellow amorphous compound obtained in the electrolysis of ammonium sulphocyanide is pseudosulphocyanogen, the yield being greatest at 50° C., and, furthermore, states that kanarin and pseudosulphocyanogen are identical.

In a still later paper, W. Markonikow (*Ber.*, xvii., ref. 279) denies that kanarin and pseudosulphocyanogen are identical bodies. In proof of this, he states that if pseudosulphocyanogen is dissolved in an equal volume of potassium hydrate diluted with twenty parts of water, it is converted into potassium sulphocyanide and potassium cyanate, while if kanarin undergoes a similar treatment, the potassium salt is obtained, which, as above stated, can be precipitated by alcohol. To prove the correctness or fallacy of these statements, the following experiments were made:—

A solution of ammonium sulphocyanide, containing 300 grms. of the salt dissolved in a litre of water, was electrolysed with a current generating 2 c.c. OH gas per minute for forty-eight hours. The yellow compound, which had separated, was filtered off and washed with hot water, until the washings no longer gave the blood-red colouration with a solution of ferric chloride, and dried at 100° C. The resulting lemon-yellow compound dissolved readily in concentrated sulphuric acid, but without any evolution of sulphur dioxide, a reaction which Markonikow gives as distinctive for kanarin. The yellow substance dissolves in potassium hydrate, more readily on heating, to a yellow solution. A portion of this solution, after acidifying with dilute nitric acid, and the addition of ferric chloride, gave not the faintest reaction for potassium sulphocyanide. To the remainder of the solution, alcohol was added. The turbidity that formed, gradually settled to the bottom of the liquid in oily drops. These were separated from the supernatant liquid by means of a separatory funnel, dissolved in water, and from this solution the lemon-yellow compound thrown out by means of hydrochloric acid. If these reactions are indicative, kanarin and pseudosulphocyanogen are identical, but the compound obtained in the electrolysis of ammonium sulphocyanide is not pseudosulphocyanogen.

The action of potassium chlorate and hydrochloric acid on ammonium sulphocyanide was also tried, the results being similar to these obtained by Miller and Markonikow with potassium sulphocyanide. The compound thus obtained has a reddish yellow colour, dissolves in potassium hydrate, the resulting solution giving a reaction for potassium sulphocyanide, and forming the potassium salt with alcohol, showing that the original substance is impure. The potassium salt, dissolved in water and treated with hydrochloric acid, now gives a lemon-yellow precipitate resembling in colour that obtained by the electrolysis of the ammonium sulphocyanide.

The author reserves for a future communication the investigation of the composition of these compounds, and in conclusion, wishes to extend his thanks to Dr. Edgar F. Smith, under whose supervision, and at whose instance, the above work was undertaken.

A New Evaporation Calorimeter.—F. Neesen.—The heat is here measured by the increase of volume which liquids undergo on passing into the gaseous state. *Zeitschrift für Anal. Chemie*, xxix., Part 4.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxii., No. 14, April 6, 1891.

Preparation and Properties of Boron Teriodide.—Henri Moissan.—The author has obtained this compound by three methods, preferably by causing gaseous hydriodic acid to react upon the amorphous boron of Deville and Wöhler. It is obtained in colourless crystals, very sensitive to the action of light. It is very hygroscopic and is decomposed by the moisture which it attracts from the air. It melts at 43° , boils at 210° , without decomposition and without giving off vapours of iodine. At a red heat it burns with a flame strongly coloured with the vapour of iodine. The specific gravity of the compound in the liquid state is 3.3 at 50° . It is very soluble in carbon disulphide and tetrachloride, and in benzene. It is less soluble in phosphorus and arsenic trichlorides and in many organic liquids. A current of 50 volts does not traverse the liquid teriodide when the electrodes are placed at the relative distance of 1 m.m. In contact with water it is at once decomposed into boric and hydriodic acids, but no iodine is liberated. It does not react with hydrogen at a cherry-red heat. If heated in oxygen it burns readily with a luminous flame, yielding iodine and boric anhydride. Melted sulphur attacks it energetically, and on contact with phosphorus in the cold there takes place a violent incandescence. With silicon it does not react. With sodium there is no action at 50° , and it may even be distilled over the alkaline metal, but at a red heat there is reaction with incandescence. Magnesium is attacked with incandescence at 500° , but aluminium not at all. Silver has no action upon the melted compound at 500° .

On a New Oxygen Compound of Molybdenum.—E. Péchard.—The addition of a few drops of oxygenated water to the solution of an alkaline molybdate produces an orange colouration which remains even if the mixture is boiled. The yellow molybdenum hydrate, $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$, though insoluble in water and acids, dissolves rapidly in oxygenated water in a gentle heat, yielding a yellow liquid. The coloured liquids thus obtained by the action of oxygenated water upon the alkaline molybdates or upon molybdic hydrate do not possess the characteristic property of molybdic liquids of giving a precipitate of ammonium phosphomolybdate in an acid solution. Oxygenated water acts also upon the alkaline tungstates. Ammonium paratungstate, sparingly soluble in water, dissolves rapidly in oxygenated water, forming a pale yellow solution. From the reactions observed the author infers the existence of a super-oxygenated acid of molybdenum, $\text{Mo}_2\text{O}_7\text{Ag}$, which he is now examining.

A New Method of Separating Iron from Cobalt and Nickel.—G. A. Le Roy.—(See p. 194).

On Dyssymmetry and the Creation of Rotatory Power in the Alcoholic Derivatives of Ammonium Chloride.—J. A. Le Bel.—If in ammonium chloride we substitute four alcoholic radicles sufficiently elevated in the series, the molecule seems to attain an invariable geometrical form, which is shown experimentally by the existence of several isomers and appearance of the rotatory power when these four radicles are distinct. The derivatives containing two equal radicles seem to take the form of an inactive isomer which cannot be split up.

On the Nitro-Derivatives of Dimethylated Ortho-anisidine.—E. Grimaux and L. Lefèvre.—These researches prove that in the action of nitric acid upon dimethylated ortho-anisidine the group $\text{N}(\text{CH}_3)_2$ affects the position of the NO_2 groups, which may take an ortho-

or a para-position like the nitro-derivatives of dimethylaniline.

On the Pyrogenous Transformation of the Campho-sulpho-phenols into Homologues of Ordinary Phenol.—P. Cazeneuve.—The passage of the phenols of the camphonic series into the aromatic series, strictly so-called, although effected in a pyrogenous reaction seems to have a real interest. The large proportions of the phenols obtained, about 25 per cent, points to a relatively simple mode of decomposition.

On Terebenthene.—Raoul Varet.—Aluminium chloride polymerises essential oil of turpentine, with simultaneous formation of cymene and other hydrocarbons.

On Ethyl Malonate and Double Ethyl Potassium Malonate.—G. Massol.—This paper does not admit of useful abstraction.

On the Micro-Organisms found on Ripe Grapes, and on their Development during Fermentation.—V. Martinand and M. Reitsch.—The microbia capable of development in an acid medium (which alone are of importance in vinification) exist in very various numbers on the surface of grapes. The moulds and the germs of *Saccharomyces apiculatus* are much more plentiful than *S. ellipsoideus*; the bacilli which produce acids and the mycoderms are not rare. The spontaneous fermentation of grapes is generally produced during the first 48 hours by *S. apiculatus*, which afterwards give place to *S. ellipsoideus*, however, without entirely disappearing. The bacteria and the mycoderms are met with not only at the outset of fermentation, but even in the lyes which renders it probable that in many cases the origin of the diseases of wines should be sought for on the skins of the grapes rather than in any subsequent contamination by the air or by the vessels.

Contributions to the Study of the Theory of Bleaching by the Air.—A. and P. Buisine.—The destruction of colouring matters is not due, as it has been hitherto supposed, simply to ozone. This body, like oxygen, whether pure or atmospheric, does not become active, i.e., capable of effecting this decolouration, except in presence of the rays of the sun. The addition of a small quantity of tallow to bees'-wax facilitates the oxidation of the colouring matter. It disappears completely during the process.

Zeitschrift für Analytische Chemie.
Vol. xxix., Part 4.

The Rise of the Freezing-Point in Mercurial Thermometers made of Jena Normal Glass.—F. Allihn.—The author's results are:—The rise of the freezing-point after prolonged exposure to ordinary temperatures amounted in the thermometers examined to a mean of 0.04° after four years. On prolonged heating to temperatures near 300° , the behaviour of the normal Jena glass is about twice as favourable as the ordinary thermometer-glass from Thuringia. For work at high temperatures the exclusive use of thermometers of Jena glass is strongly to be recommended. They should, previous to graduation, have been heated to 300° for 30 hours.

Determination of Metallic Aluminium in the Aluminium of Commerce.—G. Klemp.—Already inserted.

Determination of Moisture in Superphosphates.—Julius Stoklassa.—Already inserted.

The Examination of Water.—Dr. F. Dickmann.—The question was to ascertain whether a well had been polluted by drainage from gas-works. The substances generally sought for in such cases are ammonium salts, carbon monoxide, sulphocyanides, and cyanides, the three last being most characteristic and most readily detected. On evaporating $\frac{1}{2}$ litre of the water in order to determine

the residue, the author perceived a striking, pleasantly aromatic odour, which became more distinct on treatment with dilute hydrochloric acid. A colleague confirmed the accuracy of the perception. The author added to dry residue a few c.c. distilled water, and an equal quantity of concentrated sulphuric acid. It was not necessary to add a nitrate, as the water was rich in nitric acid. The well-known blue colour at once appeared, not extending through the entire liquid, but passing in narrow stripes from certain points to the margin. The presence of diphenylamine in the water was thus proved.

A Contribution to the Determination of the Hardness of Natural Waters by means of Soap-Lye.—E. L. Neugebauer.—The chief novelty of this process consists in the use of a special burette to which the author has given the unhappy name "titanometer," but which does not refer to titanium but to *tiranos*, the Greek word for lime.

Detection of Bile Constituents in Urine.—Dr. Adolf Jolles.—This paper will be inserted in full, if possible.

On the Determination of Foreign Crude Phosphates in Basic Iron Slags.—L. Blum.—Already inserted.

The Determination of Sulphur in Inorganic Sulphides.—L. Blum.—A claim of priority. The method of opening up pyrites in a current of oxygen put forward by J. unnasch in the *Journal für Praktische Chemie*, 1889, was described by A. Sour in 1873 in the *Zeitschrift für Anal. Chemie* (xii., 32).

On the Coefficients of Refraction of Saline Solutions.—B. Walter finds that salts may be divided into a number of groups which have different molecular refractive powers. Within a group the refractive power of a solution depends only on the number of the saline molecules present in the solution whether they belong to one or more salts if the latter only are members of the same group. There is also reference to two papers on the same subject in the *Comptes Rendus*.

The Volatility of Hydrochloric Acid.—R. B. Ward.—From the *American Chemical Journal*.

The Acceleration of Incineration in Platinum Crucibles.—H. von Jüptner (*Chemiker Zeitung*).—This paper requires the accompanying figure.

The Production of a Vacuum in an Exsiccator.—B. Franke (*Chem. Industrie*).—This paper also cannot be made intelligible without the figure.

The Acceleration of Filtration.—R. A. Fessenden.—From the *CHEMICAL NEWS*.

On Thermometer.—L. Cailliet.—From the *Comptes Rendus*.

A Gas-Balance with a Compensator.—A. Siegert and W. Durr.

A Dilatometer.—O. Knöfler (*Annalen der Physik*).

Automatic Arrangement for Turning Off Gas when the Flame Strikes Back (*Chemiker Zeitung*).—Le Roy W. McCay.—If the flame strikes back it burns a string, and the cock is closed by the release of a spring.

Mercurial Air-Pump without a Cock.—F. Neesen (*Zeit. für Instrumentenkunde*).—No particulars are here given.

A Simple Water Blast.—M. Börner (*Zeit. Angew. Chemie*).—An improvement on that of Beutell.

Diffusion of Gases through Flexible Tubing.—F. J. Smith.—From the *CHEMICAL NEWS*.

The Introduction of Two Gas-tubes into Narrow-necked Flasks.—O. Kleinstück (*Chemiker Zeitung*).—The author passes into a cork, with a single perforation, a tube with an escape-tube melted on at right angles, and introduces another tube through the latter.

Drying Apparatus for the Determination of Fats in Cattle Foods which contain Drying Oils.—O. Förster (*Land. Versuchsstationen*).—This paper requires the three accompanying couples of figures.

The Use of Hydrofluoric Acid.—E. Hart.—From the *Journ. of Anal. Chem.*

The Use of Magnesium as a Reagent.—H. N. Warren.—From the *CHEMICAL NEWS*.

Standardising a Silver Solution with Potassium Chromate as Indicator.—H. Alt (*Chem. Zeit.*).—The author uses barium chloride instead of hydrochloric acid. The barium is then removed by the addition of zinc sulphate.

Preparation of a Solution of a Ferric Salt of Known Strength.—W. French.—From the *CHEMICAL NEWS*.

The Methods for Obtaining Chlorine.—P. Klason (*Swenskhemisk Tidsskrift and Chemiker Zeitung*).—From manganese and hydrochloric acid, the best proportions, the yield obtained is 75–80 per cent of the theoretical quantity. From sodium chloride (11 parts), manganese peroxide (90 per cent), 5 parts, and sulphuric acid 14 parts the yield is 90 parts. From manganese, hydrochloric and sulphuric acids only 65 per cent. The preparation from chloride of lime and hydrochloric acid was also examined. It is not necessary to mould the chloride of lime, but this method is inferior in point of economy to the use of manganese.

Preparation and Preservation of Hydrogen Sulphides.—C. Kreuz (*Oesterreich Apotheker Vereins*).—The author fills vessels holding 150–200 c.c. with distilled water, which has been freed from air by boiling, cools rapidly, and saturates with sulphuretted hydrogen from an apparatus which has been in action for some time. The corks are cut off level and sealed with paraffin or sealing-wax.

Preservation of Sulphuretted Hydrogen Water.—A. J. Shilton.—From the *CHEMICAL NEWS*.

Separation of Barium, Strontium, and Calcium.—A. Russmann.—(An Inaugural Dissertation).

Separation of Aluminium and Zirconium.—J. Thomas Davis, jun.—From the *American Chemical Journal*.

A Reagent for Aromatic Bodies with a Hydroxyl Group at the Benzol Nucleus.—P. C. Plugge (*Archiv. der Pharmacie*).—The author recommends mercuric or mercurous nitrate containing nitrous acid. It produces a red colouration with the substances in question. He finds that benzol derivatives free from hydroxyl do not give this reaction, or not until they have been converted into hydroxyliferous derivatives.

Detection and Determination of Nitrogen in Organic Bodies.—E. Donath (*Monatshefte für Chemie*).—This paper has been noticed some time ago. Donath maintains that on oxidising nitrogenous organic matter with potassium permanganate in an alkaline solution the nitrogen is converted into nitric or nitrous acid.

The Application of Kjeldahl's Method in Hygienic Researches.—B. Proskauer and M. Zülzer.—The authors use a decomposition mixture of 800 c.c. concentrated sulphuric acid, 200 c.c. fuming sulphuric acid, and 100 grms. phosphoric anhydride. From 0.5–1.5 grm. of the sample are taken for analysis, and digested with 20 c.c. of the acid mixture, with the addition of 1 grm. mercury and 0.5 grm. anhydrous copper sulphate, until the liquid is nearly colourless. The ordinary subsequent oxidation is by adding minute crystals of permanganate. A solution of Congo-red, 1 grm. per litre, is used as an indicator.

Detection of Paraffin in Bees'-Wax.—H. Hager (*Pharm. Central Halle*).—The author's method depends on the sublimation of paraffin. The process cannot be made quantitative.

Separation of Barium and Strontium.—R. Fresenius.—The author sums up the results of a prolonged investigation as follows:—1. Barium chromate is not soluble in water containing acetic acid, if so much ammonium chromate is present that the liquid contains only alkaline acetate and bichromate. 2. Barium chromate dried at 110° is not anhydrous (as formerly assumed), but contains about 0.5 per cent of moisture. 3. Barium chromate is not decomposed on gentle ignition, and if adhering to a filter it may be weighed without loss by cautiously incinerating the filter and gently igniting the residue. 4. The determination of barium by precipitation with ammonium chromate gives results which are perfectly satisfactory. 5. The complete separation of barium from strontium by a single precipitation of the former as a chromate is not successful under any circumstances. The most favourable results obtained in this manner depend on the accidental compensation of errors of a confiding nature. 6. A complete separation of barium and strontium, and an absolutely satisfactory result in the determination of both bases can be obtained only by a twice repeated precipitation of the barium in an acetate solution with an excess of ammonium chromate; the strontium can then be thrown down first as strontium carbonate, which is then purified by conversion into the sulphate.

Band-Spectra in the Electric Arc of Carbon.—H. Kayser and C. Runge.—No particulars are given.

MEETINGS FOR THE WEEK.

- MONDAY, 27th.**—Medical, 8.30.
— Society of Arts, 8. "The Decorative Treatment of Natural Foliage," by Hugh Stannus, F.R.I.B.A.
TUESDAY, 28th.—Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, 8.30.
— Royal Institution, 3. "Bacteria: their Nature and Functions," by Edward E. Klein.
WEDNESDAY, 29th.—Society of Arts, 8. "The Use of Petroleum in Prime Motors," by Prof. William Robinson.
THURSDAY, 30th.—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "Recent Spectroscopic Investigations," by Prof. Dewar, M.A., F.R.S.
— Society of Arts, 4.30. "The Perrier Irrigation Project, Madras Presidency," by Col. J. O. Haated, R.E.
FRIDAY, May 1st.—Royal Institution, 9. "Hawks and Hawking," by James Edmund Harting.
— Royal Institution, 5. Annual Meeting.
— Geologists' Association, 8.
— Quekett, 8.
SATURDAY, 2nd.—Royal Institution, 3. "The Dynamo," by Prof. Silvanus P. Thompson, D.Sc., B.A.

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NOTICE IS HEREBY GIVEN that
HORACE KOECHLIN, of Loerrach, in the German Empire, has applied for leave to amend the Specification of the Letters Patent No. 4899 of 1881, granted to JOHN LEMAY, for "Improvements in the manufacture of colouring-matters."

Particulars of the proposed amendment were set forth in the Illustrated Official Journal (Patents) issued on the 15th April, 1891.
Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one calendar month from the date of the said Journal.

(Signed) H. READER LACK,
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THE CHEMICAL NEWS.

Vol. LXIII., No. 1640.

COMMERCIAL VALUATION OF CREAM OF TARTAR SUBSTITUTES.

By CHARLES A. CATLIN, Providence, R.I.

Few questions are more perplexing to the analyst than the commercial valuation of cream of tartar substitutes, and more especially of those containing acid phosphate preparations.

The ordinary methods of titration with standard alkali, either directly or indirectly employed, fail to give the proper data, even with the phenolphthalein indicator, as may be readily shown on taking the sample and bicarbonate of soda in the proportions thus indicated and boiling up together in water, when it will be found that the reaction is incomplete, a greater or less proportion of the carbonic acid failing of evolution, the amount varying in the same sample with the quantity of water employed, the temperature to which the mixture is submitted, and the length of time through which it endures.

Other things aside, the value of a baking acid is, of course, in its power of evolving carbonic gas from alkaline bicarbonate when in admixture therewith under the conditions in which it performs its office in the bread-making process; and since, as we have seen varying conditions have decided influence upon such reaction, it is apparent that no method of valuation can have real utility that does not take into account and, as far as possible, initiate the actual baking process in these essentials.

To inform myself more exactly, I made many careful observations of the steps pursued by a cook of the best home-spun order, in preparation of baking-powder biscuit dough and subsequent baking of the same. I found that she was using about 504 grms. of flour (Haxall brand) for the quart, as leavening for which two heaping teaspoonfuls of a popular brand of baking-powder, weighing together about 17 grms., and for moistening, 386 grms. of either milk or water, or about 23 c.c. of liquid for each gm. of baking-powder employed.

The range of temperature and the length of exposure thereto were noted as follows:—When the dough was ready for baking, a thermometer was inserted so that the bulb might be held as near as possible at the centre of the biscuit or loaf, and the whole placed in the already-heated oven by the cook in the usual manner, the range of the temperature being observed through a peephole, and record made thereof at stated times.

Averaging a series of accordant results thus obtained, I found the oven at the outset to have a temperature of about 380° F., and that the temperature of the interior of the dough passed through the following range:—

After 1 minute's exposure in the oven..	95° F.
" 3 " " " "	130° "
" 4 " " " "	150° "
" 5 " " " "	160° "
" 7 " " " "	205° "
" 10 " " " "	205° "
" 12 " " " "	210° "
" 13 " " " "	212° "
" 15 " " " "	212° "
" 17 " " " "	217° "

After thirteen minutes' exposure, the cook pronounced the biscuit "done," but for the sake of the experiment, the heating was continued when, after fifteen minutes, the crust had become far too brown to be palatable, while at the end of seventeen, actual burning had well com-

menced. From the above it is apparent, then, that in the actual baking process the temperature of the dough is raised gradually, through a lapse of about thirteen minutes, to a temperature of not more than 212° F., and for a successful issue, this should not endure for more than one minute, if indeed it should be allowed to continue for that length of time.

Consideration of these conditions of the actual baking process has led me to adopt the following method for determining the value of cream of tartar substitutes generally, and more especially of those having so-called acid phosphate as the active agent:—

The first step is to determine the neutralising power of the sample by titration with caustic alkali, using phenolphthalein as the indicator. To do this, weigh one gm. into a 300 c.c. titrating flask, run in upon it 100 c.c. of water, add 1 c.c. of phenolphthalein solution (1 gm. in 250 c.c. equal parts alcohol and water), agitate a few minutes to effect complete solution or dissemination of the sample, and then titrate with normal caustic alkali to light pink colouration. The amount of solution used to effect this is noted, a further addition is made in excess, and the whole is brought to a rapid boil and kept there for a few minutes. If now the pink colour has faded out, a further addition of alkali is made, and another moment's boiling allowed, and so on till a permanent pink colour is obtained, noting of course the alkali used. It is my custom to make these additions a cubic centimetre at a time, and in most cases I find the first excess of 1 c.c. sufficient. While the solution is still hot, add in c.c. quantities normal sulphuric acid, and then titrate back to light pink with the normal alkali. If normal solutions are used, the statement will then be:—Total alkali, less acid added, equal neutralising power of 1 gm. of sample. From this calculate equivalent bicarbonate of soda.

As there is found to be no definite ratio between the neutralising capacity of these preparations and their gas evolving power when in admixture with alkaline bicarbonate under the conditions of the baking process, and since this alone is the measure of their efficiency, their valuation should depend upon their determination of this quality. To arrive at this, weigh into a perfectly dry flask one gm. of the sample and also the exact equivalent of pure bicarbonate of soda as indicated by the titrating process. Perfectly bicarbonated soda is scarcely to be found, but it may be obtained very nearly by precipitation from a strong solution of pure mono carbonate supersaturated with carbonic acid, drying the salt with bibulous paper as far as possible, then powdering, and finally drying over oil of vitriol, under a bell glass, in the ordinary manner. Thus prepared, it is hardly necessary to make allowance for the slight trace of monocarbonate which seems to be all but unavoidable. Its carbonic acid strength should be carefully determined, however, for accurate work. The flask, fitted with the usual stoppered funnel and exit tube, into which has been weighed the charge of sample and its equivalent bicarbonate, is attached to a carbonic acid absorption apparatus of any of the well known types.

Personally I much prefer the soda-lime tubes to the potash bulb, but this is a matter of individual experience.

In the actual baking process, we found that 23 grms. of water were employed for each gm. of baking-powder used. A large part of this water must have been practically inert in bringing about reaction between the constituents of the powder, being absorbed by the flour. Just what that loss of water would be we have not the means of determining, but certainly not more than half the water employed can be considered as exerting solvent action upon the powder. I would therefore recommend that not more than 20 c.c. be used for each gm. of acid sample and its soda bicarbonate equivalent. A very much larger amount would so alter the conditions of reaction that unreliable results would be the consequence. A very much smaller amount would be impracticable to use. In the flask, after attaching the absorption apparatus, introduce therefore through the funnel tube 20 c.c. of water,

and disseminate the powder through it by careful agitation of the whole. We have seen in our observation of the baking of the biscuit, that in the matter of temperature, 212°F. is never exceeded within the dough in proper manipulation, and that limit should never be allowed to endure for more than one minute at the longest. As a matter of fact, I believe that when the temperature reaches 200°F. , or even a much lower point, the dough has attained such a consistency that further evolution of gas is rather an injury than an advantage. However this may be, it is certain that gas evolved beyond the limit of a temperature of 212°F. , enduring for one minute, is of no practical value. The contents of the flask is therefore gradually raised to the boiling-point, and as we have observed in the baking process, maintained at that temperature not longer than one minute, then aspirate the flask and note the increased weight of the absorption tubes, which gives us then the amount of carbonic acid evolved under the baking conditions, and is consequently the correct measure of strength of the sample for the purpose for which it is designed. Knowing the carbonic acid contents of the bicarbonate of soda used, the results obtained as above may be readily checked by again attaching the absorption tubes to the flask and running in through the stoppered funnel a few c.c. of dilute sulphuric acid, whereby the remaining carbonic acid will be evolved. Aspirating the apparatus again, the total increase in weight of the absorption tubes above the first weighing should correspond with the calculated amount of carbonic acid in the bicarbonate of soda used.

This last step suggests a more rapid method of procedure:—

Find the neutralising power of the sample as before, then into the flask of the carbonic acid apparatus weigh one gm. and its equivalent bicarbonate of soda, add the 20 c.c. of water, bring the whole to a boil, and keep it at that temperature not longer than one minute, the flask being detached from the absorption tubes meanwhile, blow out the flask to remove all of the carbonic acid thus evolved, then attach to the absorption apparatus and determine the carbonic acid still remaining unevolved by adding the dilute sulphuric acid, &c., as before. The carbonic acid thus obtained, deducted from the total calculated carbonic acid of the bicarbonate of soda employed, gives the gas-evolving power of the sample under the conditions of the baking process.

For a convenient statement of results I would suggest taking the carbonic acid equivalent of one gm. of pure bitartrate of potassium, i.e., 0.2340 gm., and expressing results in thousandths of that standard, obtained by removing decimal point, adding three 0 to the amount of carbonic acid carried to tenths m.grms., and dividing by 2340.—*Journal of Analytical Chemistry*, iv., Part 4.

ON U. GAYON'S ALDEHYD REACTION.

By H. BORNTRÄGER.

For the detection of aldehyd with spirit U. Gayon (*Comptes Rendus*) proposes a solution of magenta which has been previously decolourised by the addition of a little hydrochloric acid and much sodium bisulphite. The writer has used this reaction for about two years, and concludes from his experience that it is fundamentally useless for the purpose in question, from the following reasons:—

The solution is in a short time turned red again by atmospheric air, in consequence of the presence of ozone, hydrogen peroxide, nitrous acid, &c. (possibly by oxygen alone); a phenomenon which may be observed on the stopper of the bottle, since the bisulphite (the decolourising agent) is converted into bisulphate when the colour of magenta reappears. This change occurs immediately in presence of aldehyd or of oxidising agents such as chlorine and the nitrogen oxides,

On the other hand, the magenta colour is at once destroyed by acetyl, which is present in every spirit which has not been well rectified, especially in Russian samples; so that if little aldehyd and much acetal be present, the above reaction will take place very feebly or not at all.

The reaction, therefore, can only show whether the spirit contains appreciable quantities of oxidising agents or not.

We might therefore, as in the case of spring-water, speak of "oxidisability."

This reaction, though very sensitive, is quite unfit for a quantitative determination. The only certain reactions hitherto known for aldehyd, when moderately diluted, are its power of reducing ammoniacal solutions of silver and ammoniacal permanganate, which, unfortunately, hold good only if the aldehyd is present in sufficient quantity.

All other reactions are untrustworthy, as they indicate a variety of substances.

The author is hitherto not aware of any certain reaction for detecting traces of aldehyd in spirit.—*Zeit. Anal. Chem.*, xxx., p. 208.

THE DETERMINATION OF MANGANESE IN IRON AND STEEL.

By L. BLUM.

L. RÜRUP recently made known (*Chemiker Zeitung*) a method for the determination of manganese in iron and steel, said to be a modification of the Volhard process, calculated to economise time.

Six grms. of the material are weighed out, placed in a litre flask, after being dissolved and oxidised, neutralised, mixed with sodium sulphate, filled up to the mark, and filtered through two folded filters. Of the filtrate, 500 c.c. are placed in a one-litre Erlenmeyer flask, mixed with zinc oxide, heated, and titrated with permanganate.

In an editorial remark in the *Chemiker Zeitung*, attention is called to the differences which arise from neglecting the volume of the precipitate of basic ferric sulphate. The author now points out two other defects in the method calculated to affect the accuracy of the results.

According to Volhard, the exact conversion of a manganous salt into a hydrated manganese peroxide by the action of permanganate ensues only if another strongly basic oxide is present in solution. For this purpose he found zinc oxide the most suitable. Meinecke further showed that considerable quantities of zinc sulphate—25 to 30 grms.—must be present in order to effect the intended purpose. As in Rürup's modification its presence is excluded, the precipitate formed on titration will always contain manganous compounds, thus rendering the consumption of permanganate too small.

A further defect, which tells in the same direction, lies in the presence of free zinc oxide. On this point Meinecke has made careful investigations, and has ascertained that a deficient consumption of permanganate, and consequently reduced result, is in direct connection with the presence of undissolved zinc oxide.

These facts speak decisively against the adoption of Rürup's modification, especially as in Volhard's method, as used in metallurgical laboratories, a determination of manganese can be conveniently completed in three-quarters to one hour.—*Zeit. Anal. Chem.*, vol. xxx., p. 210.

COLOURED REACTIONS OF THE AROMATIC AMINES.

By C. H. LAUTH.

THE author has recently shown that on treating dimethylaniline acetate with lead peroxide we obtain a fine and very intense green. This reaction, if applied to other aromatic amines, gives in a great number of cases very

	In presence of H ₂ O.	In presence of alcohol.
Aniline	Fugitive violet-red, then red-brown.	As with water.
Monomethylaniline	Blue-green, then violet, blue, and finally olive.	Violet, red-violet, olive.
Dimethylaniline	Orange, grass-green, olive-green, grey.	Orange-green.
Monoethylaniline	Blue-green, blue, violet, olive.	Violet, violet-black, olive.
Diethylaniline	Bright orange, yellow.	Greenish yellow.
Benzylaniline	Red-brown, reddish violet, grey.	Yellowish grey, green.
Methylbenzylaniline	Orange, greenish yellow, greyish green.	Bright green, blue-green-violet.
Ethylbenzylaniline	Orange.	Olive, bright green-olive.
Diphenylamine	Violet grey, not intense.	Bright green, olive.
Methyldiphenylamine	Magenta, violet-brown.	Violet-brown.
Paratoluidine	Blood-red, brown-red.	Bright blood-red.
Orthotoluidine	Dragon-green, violet.	Red-violet, brown-violet, orchil.
Dimethylparatoluidine	Green-brown, dirty yellow.	Green-brown, dirty yellow.
Dimethylorthotoluidine	Bright orange-red, orange-brown.	Green-brown olive.
Xylidines		
" meta α	Violet-blue, grey-black.	Very red-violet, orchil.
" β		
" mixture of ortho and para ..		
Paraphenyldiamine	Bright blue-green, brown.	As with water.
Metaphenylenediamine	Brown.	Brown.
Dimethylated paraphenylenediamine ..	Magenta, violet-blue, violet-black.	As with water.
" metaphenylenediamine ..	Slight yellowish brown.	Yellow-brown.
Toluenediamine (from binitro)	Bright red-brown.	As with water.
Naphthylamine α	Slight violet-blue.	As with water.
" β	Slight yellow-brown.	Slight red-brown.
Dimethylnaphthylamine α	Bright madder red, dull white.	Madder red.
Benzidine	Intense pure blue, violet, red.	Yellow, with a blue precipitate.
Tetramethylbenzidine	In presence of excess of acid, grass-green with an orange cast.	Grass-green.
Dimethylated ortho-anisidine	Violet magenta, dirty violet.	Green-grey, olive.
" meta-anisidine	Yellowish brown.	Yellow-brown.

distinct colourations, and, as a trace of the product is sufficient for their development, they may serve to characterise such bases when present only in very small quantities.

The author puts in a watch-glass a drop of the amine in question or, if solid, a corresponding quantity of the crystals. He adds 10 drops of a solution containing 3 vols. of acetic acid at 8° and 7 vols. of water. The base generally dissolves under these conditions, though a perfect solution is not required, as the coloured reactions are more distinct with an excess of the base than with an excess of the acid. It is well to make simultaneously a blank experiment with an alcoholic solution of acetic acid at the same degree of dilution. Certain bases are, in fact, insoluble in aqueous acetic acid, and, on the other hand, we sometimes obtain in presence of alcohol different colourations due to the action of its oxidation products, especially aldehyd. On the slopes of the watch-glass he spreads out some particles of "pure oxide" (lead peroxide?), then, inclining the glass a little, the acetic solution is brought in contact with them. The accompanying Table gives the most characteristic colours and their changes.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MARCH 31ST, 1891.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, April 7th, 1891.

SIR,—We submit herewith the results of our analyses of the 168 samples of water collected by us during the past

month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined, the whole were found to be clear, bright, and well filtered, excepting 3, which were recorded as "very slightly turbid."

We observed at the conclusion of our previous Report that towards the end of the month of February, the water furnished alike by the several Companies had all but recovered its habitual character, and freedom from turbidity and colour. That this improvement was well sustained throughout the succeeding month of March is shown by a comparison of the Thames-supply results afforded during the month of March with the mean results obtained during the six months, July to December, 1890, distinguished as this period was by the exceptionally high character of the water supply generally:—

Thames-derived Supplies.

	July—Dec., 1890.	March, 1891.
Ratio of brown to blue tint ..	Means 13.5 : 20	14.1 : 20
Oxygen required for oxidation ..	" 0.049	0.049
Organic carbon per 100,000 ..	" 0.144	0.146
" " " ..	Maxima 0.170	0.209

The maximum proportion of organic carbon, namely 0.209 part in 100,000 parts of the water, corresponding roughly to about three-eighths of a grain of organic matter per gallon, was met with in a single sample only,

the two next highest results amounting to but 0.162 part and 0.161 part respectively in 100,000 parts of the water.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

CONCERNING THE PENTAGLUCOSES.*

By W. E. STONE.

THE two isomeric sugar-like bodies, arabinose and xylose, with the common formula $C_5H_{10}O_5$, corresponding in many characteristics to the true glucoses and in others quite distinct from the latter, may be referred to collectively as *pentaglucooses*. This term expresses the relation between these compounds and the true, or hexaglucooses, and has already become established by some degree of use† (*Ber. d. Chem. Ges.*, xxi., 2151; xxii., 1046; xxiii., 137, 1751; *Ann. Chem. (Liebig)*, ccxlix., 227; ccliv., 304; *Am. Chem. Jour.*, xii., 435, &c.).

The two bodies just mentioned are the only members of this group thus far observed. Of these, arabinose has been known for more than twenty years, but was regarded until within a short time as a true glucose; while xylose is a recent discovery (Koch, *Pharm. Ztschr. f. Russland*, xxv., 619, &c.), and has also been shown by Tollens and his pupils to be a pentaglucoose (Tollens and Meyer, *Ber. d. Chem. Ges.*, xxi., 647; Tollens and Wheeler, *Ann. Chem. (Liebig)*, ccliv., 304).

The pentaglucooses are strictly sugar-like bodies, crystalline, sweet, reducing Fehling's solution, and dextro-rotatory. In some respects, however, they differ decidedly from the true glucoses. They are not subject to alcoholic fermentation, as has been previously proven for arabinose (*Ann. Chem. (Liebig)*, ccxlix., 257), and as I am now able to announce for xylose. As a distinctive and specific reaction, the pentaglucooses produce large quantities of furfural when subjected to the action of strong acids, and in this way are sharply separated from the true glucoses, which, under similar conditions, yield levulinic acid (*Ber. d. Chem. Ges.*, xxi., 2150; *Ann. Chem. (Liebig)*, ccxlix., 227). By perfected methods the amount of furfural thus obtained amounts to nearly fifty per cent when pure arabinose or xylose is used (*Ber. d. Chem. Ges.*, xxiii., 1751).

The pentaglucooses have not been observed as occurring in nature, but are obtained by hydrolysis of certain plant constituents. These mother-substances are found either normally as a part of the cellular tissues of the plant, or in some notable examples as abnormal gum-like secretions. So far as is known, the substances occurring under either of the above conditions are identical, although at the present time we have no means of distinguishing between those substances which will yield arabinose from those which will yield xylose.

Arabinose has been prepared from the cellular tissues of the sugar beet (*Ibid.*, i., 58, 108), from gum arabic (*Ibid.*, vi., 612), gum tragacanth (Sachse u. Martin, "Phytochemische Untersuchungen"), cherry gum (*Ibid.*), and from wheat bran (*Ann. Chem. (Liebig)*, ccxlix., 239; also *Ber. d. Chem. Ges.*, xxiii., 3110). Xylose has been obtained from woods of different species and jute (*Ann. Chem. (Liebig)*, ccliv., 304), and from straw (*Ber. d. Chem. Ges.*, xxiii., 137). From brewers' grains, i.e., from the outer seed coats of barley, both arabinose and xylose have been prepared (*Ann. Chem. (Liebig)*, ccxlix., 243), while from peach gum arabinose and galactose were ob-

tained (*Am. Chem. Jour.*, xii., 435), and gum arabic also would seem to contain the mother-substances of arabinose and galactose.

The nature of this substance, or these substances, from which the pentaglucooses are derived is not well understood. They are of a gummy nature and may be spoken of comprehensively as *gums*, a term clearly applicable in some cases but less so in others. In normal woody tissues, for instance, it is difficult to locate any material of the nature of gums, but by means of alkalis an amorphous substance may be extracted which is insoluble in water, alcohol, and ether, and which by the action of acids may be converted into one or other of the pentaglucooses. This substance has been variously designated as metapectic acid, arabin, wood gum, &c. Tollens and Allen have pointed out that the occurrence of this gummy material *in situ* corresponds closely to the lignin reaction with hydrochloric acid and phloroglucin (E. W. Allen, "Inaugural Dissertation," Göttingen, 1890). Moreover, E. Schulze has lately shown that preparations of cellulose, which, according to all appearances, were pure, still gave the lignin reaction and yielded an appreciable amount of furfural (*Ber. d. Chem. Ges.*, xxiii., 2579), indicating that these substances are most intimately connected with the ultimate cellular tissue, from which they are separated with difficulty. Wherever these gums occur, they may be recognised by the furfural reaction which characterises the pentaglucooses. In this reaction, the pentaglucooses are doubtless formed as an intermediate product, and themselves eventually yield furfural. The furfural test may therefore be applied to any crude material as a means of detecting the presence therein of these gums, which by proper treatment yield the pentaglucooses. Indeed, the search for, and ultimate preparation of, arabinose and xylose from several of the materials mentioned has been based upon the results of a preliminary furfural test.

The continuation of my studies beyond this point, as described later, will perhaps increase the interest and importance attached to this group of bodies.

A.—Occurrence of the Pentaglucooses.

The reliability of the furfural reaction as indicative of the presence of the pentaglucooses, or the gums from which they are derived, having been established, and having led to the preparation of arabinose and xylose from several unexpected sources, the question naturally followed: how frequently do these bodies occur in vegetable products, or how widely diffused may they be in nature? Strictly speaking, only the gums are found under these conditions; but since they are little known except in their derivatives, the pentaglucooses, to which they seem to stand in direct relation, we may regard the former as representing the occurrence of the latter. If occurring commonly, they still find no recognition in our present analytical methods, towards which their reactions are those of the normal carbohydrates and glucoses. In the case of foods, results thus obtained may give rise to erroneous estimates of the values of certain materials, since we have no ground for assuming that the two classes are of equal or even similar nutritive value.

I have therefore examined a considerable variety of vegetable materials, including different parts and products of plants, for the purpose of detecting the presence of these gums as indicated by the production of furfural when treated with strong acids. The list of materials might be greatly extended, but it suffices, perhaps, to show that these bodies are much more widely and abundantly distributed than is ordinarily supposed.

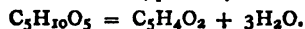
The method of making these tests is practically the same as that used in the original study of the reaction. It allows of a comparison of the amounts of furfural produced from different sources under fairly constant conditions. The results, however, are not absolutely quantitative, failing to yield the highest possible amount of furfural in comparison with the method proposed by

* Contributions from the Chemical Laboratory of Purdue University. From the *American Chemical Journal*, Vol. xiii., No. 2.

† E. Fischer proposes a numerical nomenclature for the different series of sugars so notably extended by his syntheses, according to which this group are called the "*pentoses*." This is perhaps preferable to the term here used, and may find adoption eventually.

Tollens and Günther (*Ber. d. Chem. Ges.*, xxiii., 1751). Having commenced these studies, however, some time since, I have preferred to retain the original method, for the sake of comparison between earlier and later results. This method is as follows:—

2—5 grms. of the finely powdered air-dried material are placed in a flask of 200—300 c.c. capacity, with 50 c.c. of sulphuric acid of 1.254 specific gravity. The flask is then placed in a paraffin bath and connected with a condenser; through a second opening in the stopper, connection is made with a reservoir from which water is allowed to drop into the flask with just sufficient rapidity to replace the loss by distillation and thus maintain a constant concentration of the acid. The bath is heated to 125—135° C. The first action of the acid is to convert the gums into pentaglucozes, followed at once by the decomposition of the latter, probably in this way,—



The furfural thus formed is distilled over and collected. This distillation is continued so long as there is evidence of the presence of furfural in the distillate. This evidence is furnished by a reaction which is very delicate, and which consists in allowing a drop of the distillate to fall on a strip of filter paper moistened with aniline acetate. So sensitive is this reaction that one part of furfural in one hundred thousand parts of water produces instantly an intense red colour upon the paper. In more concentrated solutions this colour becomes darker and eventually reddish brown.

Usually eight to ten hours are required to complete the distillation, and the distillate amounts to 200—300 c.c. The furfural contained therein is next concentrated, by fractional distillation, to a volume of 3—6 c.c., in which it may in part appear in the form of light yellow oily drops. Upon the addition of dilute ammonia, a precipitate of furfuramide is formed, which is collected, dried over sulphuric acid, weighed, and the relation of its weight to that of the original material calculated in percentages. The following results therefore express the amount of furfuramide obtained from the various materials. But 1 gm. of furfuramide theoretically requires for its production 1.6875 grms. of a pentaglucoze, and practically,

	Per cent of furfuramide.
Hungarian grass	3.34
Timothy hay	1.18
Cornstover, I.	2.89
" II.	1.48
Maize ensilage	0.91
Clover hay	1.55
Clover ensilage	0.40
Wheat straw	4.16
Oat straw	2.29
Malt sprouts	1.82
Brewers' grains	7.20
Corn bran, I.	0.84
" II.	1.80
Linseed meal	1.20
Corn and cob meal	0.59
Corn cobs	8.16
Oatmeal	0.40
Beet pulp	3.59
Cotton-seed hulls	3.66
Pulp of strawberries	1.95
Dung of cattle fed on maize ensilage	2.88
" " corn stover	3.94
Gum arabic	5.46
Cherry gum	8.14
Gum tragacanth	8.08
Peach gum	4.84
White lupine seeds	0.95
Yellow " "	1.69
Coats of orange seeds	1.35
Orange peel	0.69
Watermelon seeds	2.70

under the conditions described, rather more. Hence the percentages given may be multiplied by the above factor (1.6785), and will then indicate less than the actual amount of pentaglucozes present. From about forty substances examined, thirty-one yielded appreciable amounts of furfuramide (see Table).

The following materials yielded no perceptible quantities of furfuramide, but all gave strong qualitative reactions for furfural, and it is hardly too much to expect that with a better method of distillation these also might yield furfural in noticeable amounts:—

Dried strawberries,
Cotton-seed cake,
Corn meal,
Dried sweet potato,
Kernels of orange seeds,
Raw coffee,
Buckwheat,
Beans.

Under the stated conditions, these results, indicating that in more than three-fourths of these materials, taken at random, there exist the equivalents of from 1 to 12, or more, per cent of pentaglucozes, plainly prove the common and abundant occurrence of the latter. It is evident, therefore, that among the vegetable products usually classed as carbohydrates the pentaglucozes, or the gums giving rise to them, play an important part.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Annual General Meeting, March 25th, 1891.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

THE President delivered an address, of which the following is an abstract:—

The number of Fellows is 1786, of whom 32 are honorary foreign members. One foreign member, Dr. Heinrich Will, and 17 Fellows have died during the year:—Dr. M. Bechler, W. Blythe, H. B. Brady, F.R.S., C. I. Burton, W. Lant Carpenter, T. Carnelley, J. B. Hutcheson, J. A. Hill, Robert MacCalmont, E. C. Nicholson, T. R. Ogilvie, C. P. Phillips, H. Poland, H. Smith, W. C. Stevens, F. O. Landell, and H. H. Walker.

The following 13 Fellows have withdrawn:—A. Bain, E. N. Butt, J. Barker, R. Carruthers, W. H. Glazier, J. Hall, A. E. Johnson, E. A. Parnell, W. E. Porter, W. R. Reffell, J. Stokes, A. Taylor and R. C. Tresider.

28 Fellows have been removed from the list on account of arrears:—B. Akroyd, H. J. Alford, P. H. Cathcart, F. W. Dupré, A. F. Darnon, H. Eccles, W. T. Elliott, J. W. Ellis, M. P. Gossett, E. Ernest Graves, T. F. Garwin, T. Hart, W. H. Hyatt, F. H. Lowe, H. A. B. Leipner, T. Muskett, F. Nettlefold, C. O'Keefe, L. Peckitt, G. F. Rodwell, V. P. Richards, A. H. F. Ruppell, A. E. Simpson, W. F. K. Stock, C. A. Smith, P. C. Thomas, Dr. W. H. Wilson, and W. A. Wren.

114 Fellows have been elected during the year, being 31 fewer than last year.

The financial state of the Society is not quite so satisfactory, said the President, as it has been for some years past, the receipts from subscriptions being £177 less than last year. This falling off is to be accounted for partly by the accidental circumstance that there were 11 fewer life compositions than last year, but chiefly by the fact that no fewer than 26 candidates had been blackballed.

The same number of papers, viz. 72, have been printed in the *Trans. Chem. Soc.* as last year, but they occupy no fewer than 1051 pages, instead of 772 pages in the previous year. There has been a considerable increase

in the number of abstracts, 2341 appearing this year and occupying 1527 pages, whereas last year the number was 2131, which occupied 1252 pages. Hence the cost of the Journal has been greater this year by £413.

All the new and valuable works on chemistry have been added to the Library as they were published.

The time had again come round for the award of the Longstaff medal, given every third year to the Fellow of the Society who, in the opinion of the Council, had done the most to promote chemical science by research. This instruction was not always easy to carry out; but the unanimous decision arrived at on this occasion to award the medal to Professor Japp would certainly, he thought, be regarded by the Fellows generally as eminently satisfactory. All who followed the higher development of organic chemistry knew how valuable were the carefully thought-out papers which Professor Japp had communicated to the Society. It was a matter of regret that he was unavoidably prevented attending the meeting to receive the medal in person.

The great event of the year had undoubtedly been the celebration of the Jubilee on February 24th and 25th; it was the intention of the Council to issue in a separate form a full account of the proceedings on these occasions. With reference to the reception held at Goldsmith's Hall on the evening of the 24th by the President and Council, the Goldsmiths' Company had not only lent their Hall for the occasion, but with that liberality for which the great City Companies were so noted, "recognising that the occasion was of quite an exceptional character," had expressed their wish to relieve the Society from the expense attending the preparation and use of the Hall.

The suggestion made in his previous address that a subject catalogue of the Journal from its commencement might be published as a fit memorial of the Jubilee had, he thought rightly, been abandoned, as it appeared that the labour and expense involved would be greater than the result would justify.

It seemed appropriate to the occasion to briefly chronicle the changes which had occurred in the constitution and government of the Society since its foundation. Little or no alteration of bye-laws or plan of working the Society occurred during the early years. In 1852 the number of Vice-Presidents, which was then four, was increased by adding all past Presidents; but it was not until 1866 that any other change worth recording took place. In that year a new form of nomination paper was introduced, and this seems to be the first indication of any feeling having arisen that undesirable people were seeking and obtaining admission into the Society: this question had from time to time caused more discussion among the Fellows than any other relating to the government of the Society.

As chemistry became of more public importance, a very natural impression gained ground that, since all the more distinguished chemists of the day belonged to the Society, therefore every Fellow must be a thorough chemist. This misconception on the part of the public had had a most mischievous effect. In 1867 the matter was very fully discussed, and was ultimately referred by the Council to a committee consisting of Mr. Crookes, Dr. Miller, Dr. Odling, Mr. Wanklyn, and Dr. Williamson. The report of this committee was adopted and sent to all the Fellows, and it stated the case so fully that it appeared well to republish it on the present occasion. This committee decided not to recommend "any alteration in the bye-law relating to the election of Fellows which would have the effect of confining the Fellowship of the Society to strictly scientific men." But with a view to increase the security against the election of undesirable candidates, they recommended that the number of signatures attached to a certificate be five instead of three, three instead of one to be from personal knowledge. The recommendations were adopted, and appear to have met the requirements of the case, as the agitation ceased.

In 1877 another similar outbreak took place, but on this occasion the feeling that it was practically impossible for the Society to insist on all its Fellows being trained and competent chemists became so strong that ultimately it was decided to found the present Institute of Chemistry.

Now, after the lapse of 14 years, a discussion is again raised, but the collateral circumstances are very different, as, through the existence of the Institute, all who desire to be stamped as educated chemists have the opportunity of obtaining such recognition. It was, however, necessary to arrive at a clear understanding as to who we desire to attract, and who we desire to exclude from our Society. Speaking for himself, said the President, he should wish to see the entrance made easy for all who have any real interest in our science, even if they be only amateur chemists, provided that socially there be no objection to their admission; he would entirely abandon the idea that amount of chemical knowledge is to determine the suitability of a candidate.

It was practically impossible by any hard-and-fast rules to exclude undesirable persons, and the history of the Society went to show that the only effective method was for the Fellows themselves to realise that it rested with them to recommend only proper persons.

What had been the history of the Society during the past 14 years as showing whether the means at disposal had been effective in securing the prosperity of the Society? Without a shadow of doubt the Society never stood so high both in the scientific and external world as at the present time; his experience during the past two years had shown him how widely the Society was known, and in how favourable a light it is regarded at home and abroad.

If the feeling be cultivated and generally acknowledged that the body of Fellows expect and require that all should act honestly and honourably towards one another, there will be very few improper persons gaining admission. On learning that any Fellow is acting in any way wrongly or dishonourably towards the Society, the first thing in future will be to ascertain, by reference to the *Proc. Chem. Soc.*, who are the five Fellows who certified that the said Fellow was a proper person to join the Society. Nothing is more powerful than public opinion, and if it be felt that such a spirit should guide all elections, far more good will accrue to the Society than any law can effect which can be invented or enforced.

Dr. GILBERT proposed a vote of thanks to the President, coupled with the request that he allow his address to be printed; the motion was seconded by Mr. CARTEIGHE. Both speakers referred in most appreciative terms to Dr. Russell's services to the Society, especially on the occasion of the Jubilee celebration. Dr. TEED supported the motion, which was carried by acclamation. The President having acknowledged the vote,

Professor THORPE, the Treasurer, gave an account of the financial position of the Society. The receipts from Fellows had been £3459 16s.; from sale of the Journal £383 9s. 4d.; and by dividends on invested capital £363 0s. 6d. The expenses on account of the Journal had been £2724 0s. 10d.; on account of the Library £300 18s. 9d.; on account of the *Proceedings* £183 7s. 10d.—the total expenditure being £3790 4s. 9d. The balance at the bank was £1798 17s. 7d.; and £600 had been invested in Metropolitan Board of Works 3½ per cent stock.

Professor ATTFIELD proposed that the thanks of the Fellows be tendered to the Treasurer. Dr. ATKINSON, in seconding the vote, lamented the loss of income during the year, and referred to the smaller expenditure out of the Research Fund, and the excessive balance at the bank.

Dr. STEVENSON advocated a larger expenditure on the Library. Mr. FRISWELL followed Dr. Atkinson in lamenting the diminution in income and its cause, and also referred to the disproportion borne by the life composition

fee to the annual subscription. Mr. CASSALL asked that increased facilities of using the Library might be granted to Fellows.

The PRESIDENT said that every effort was made by the Library Committee to obtain books, and that if Dr. Stevenson and others who complained of deficiencies would point out what was required, the Library Committee would most certainly pay the utmost attention to their recommendations. The Library would be open at any reasonable and rational time. [Dr. THORNE subsequently stated that the statistics of attendance on evenings other than those when meetings took place in the buildings, were such as to indicate that there was no great desire to use the Library in the evenings]. It so happened that a considerable sum had been voted out of the Research Fund at a time just outside the financial year, so that actually the expenditure was greater than appeared.

The TREASURER, in acknowledging the vote of thanks, said that the large balance would very soon disappear, as a number of heavy payments had to be made. He took occasion to gratefully acknowledge the service which Mr. Tutton had rendered him in keeping the Society's accounts, and finally proposed that thanks be given to the Auditors, Messrs. H. Crompton, R. H. Davies, and B. Dyer. This proposal was seconded by Dr. COLLIER and adopted. Mr. DYER having replied,

Professor RAMSAY moved a vote of thanks to the Officers and Council, which was seconded by Mr. FRISWELL, and acknowledged by Dr. ARMSTRONG.

Mr. WARINGTON finally proposed that thanks be tendered to the Editor, Sub-Editor, Abstractors, and Librarian. Dr. CLOWES seconded the motion. Mr. GROVES and Dr. THORNE replied.

Scrutators having been appointed, a ballot was taken, and as result the following were declared elected as Officers and Council for the ensuing session:—

President: Dr. A. Crum Brown, F.R.S.

Vice-Presidents who have filled the office of President:

Sir P. A. Abel, K.C.B., D.C.L., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: G. Carey Foster, F.R.S.; W. N. Hartley, F.R.S.; John Pattinson; J. Emerson Reynolds, M.D., F.R.S.; William A. Tilden, F.R.S.; Robert Warington, F.R.S.

Secretaries: H. E. Armstrong, Ph.D., F.R.S.; J. Millar, Thomson, F.R.S.E.

Foreign Secretary: Raphael Meldola, F.R.S.

Treasurer: T. E. Thorpe, B.Sc., F.R.S.

Ordinary Members of Council: E. Atkinson, Ph.D.; Henry Bassett; Norman Collie, Ph.D.; John Ferguson, M.A.; E. Kiuch; M. M. P. Muir; F. J. M. Page; W. H. Perkin, jun., F.R.S.; S. U. Pickering, M.A.; Boverton Redwood; Thomas Purdie, B.Sc.; John A. Voelcker, Ph.D.

The meeting then proceeded to consider the alterations in the bye-laws proposed by the Council. The first alteration having been read to the meeting,

Mr. LLOYD asked the President what would be his ruling with reference to any new proposal made at the meeting to alter the bye-laws.

The PRESIDENT said that he could not allow any proposal to alter the bye-laws of which notice had not previously been given to the Fellows to be put at that meeting. Although there was no express provision to that effect either in the charter or bye-laws, it was manifestly inexpedient to adopt any other course, and such ruling would be in accordance with the practice of the Society hitherto.

Mr. LLOYD stated that the movement in which he and

others had taken part had for its object to exclude those who were personally objectionable, and to effect this they desired to place the nomination of Fellows in the hands of the Council. He therefore moved as an amendment that the whole subject of the alterations in bye-laws be postponed.

The PRESIDENT having ruled this amendment out of order, after a few remarks from other speakers, a vote was taken, and the following alteration in the bye-laws was carried, there being only five dissentients:—

"That in the case of candidates resident abroad unable to obtain the before-mentioned number [five] of signatures, the Council shall have power to accept a certificate signed from personal knowledge by one Fellow of the Society, and to recommend its presentation for ballot."

Subsequently the following were also put to the meeting and carried all but unanimously:—

2. That the following notice be printed at the head of the Form of Recommendation:—

"The attention of the candidate in whose favour this certificate is made out is specially directed to the fact that, if elected, he will be required to sign the following obligation prior to his admission into the Society:—

"Obligation.—I, the undersigned, do hereby engage that I will endeavour to promote the interests and welfare of the Chemical Society, that I will observe its laws, and to the utmost of my power maintain its dignity, as long as I shall continue a Fellow thereof.

3. That Bye-law XII. be altered so that it read as follows:—

"An Annual General Meeting of the Society shall be held on the 30th day of March, or on some day in March near that time, and at such an hour as the Council may determine, for the election of Officers, &c."

April 2nd, 1891.

WILLIAM CROOKES, F.R.S., Vice-President, in the Chair.

CERTIFICATES were read for the first time in favour of T. St. John Belbin, 12, Bolton Mansions, South Kensington; James Lane Natter, Leigh Grange, Woolstone, Southampton; Frederick Tetley, 3, Mannville Terrace, Horton Road, Bradford.

The following papers were read:—

1. "*Citraconfluorescein*." By J. T. HEWITT, B.A., B.Sc.

With the object of further comparing citraconic with maleic anhydride, the latter having been shown by Lunge and Burckhardt to be capable of yielding a fluorescein, the author has submitted citraconic anhydride to the action of resorcinol in presence of sulphuric acid, and finds that, like maleic anhydride, it yields the corresponding fluorescein. Citraconfluorescein is readily soluble in alcohol and glacial acetic acid, and fairly soluble in water; the aqueous solution is of a yellowish-brown colour, and exhibits a green fluorescence less vivid than that of ordinary fluorescein.

2. "*Ethylic Thiocetacetate*." By C. T. SPRAGUE, B.Sc., Ph.D.

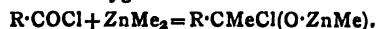
The author describes a series of experiments made with the object of determining the constitution of the ethylic thiocetacetate which Hübner obtained by the action of sulphur monochloride, S_2Cl_2 , on ethylic acetate, and which, after his death, was studied by Buchka. The same substance has since been prepared by Deliole by the action of sulphur dichloride, SCl_2 , on ethylic acetate; by Schönbrodt by the action of sulphur on the copper derivative of ethylic acetate; and by Michaelis and Phillips from thionyl chloride and ethylic acetate. Buchka proposed the formula $S(CH_3Ac \cdot CO_2Et)_2$, but an alternative formula $S(O \cdot C \cdot CH_3 \cdot CO_2Et)_2$, was suggested by Deliole.

After describing the preparation of the substance, the author discusses the discrepant statements made by

different observers as to its melting-point. He then describes at length the products of the interaction of hydrazines and ethylic thiocetate, and shows that it behaves towards phenylhydrazine, &c., in the same manner as ethylic acetate: in the first instance, a pyrazolone sulphide is formed from 2 mols. of the hydrazine and 1 of the thiocetate; the sulphides are in the next instance converted by further action of the hydrazine into pyrazolone disulphides and bisphenylmethylpyrazolone or the homologous substances; and, finally, the pyrazolone disulphides and the hydrazine interact to form hydrogen sulphide and hydrazones of the pyrazole series. The results afford further proof of the correctness of Buchka's formula.

3. "The Function of Chlorine in Acid Chlorides as Exemplified by Sulphuryl Chloride." By HENRY E. ARMSTRONG.

A large number of experiments carried out during recent years in the author's laboratory show that sulphuryl chloride, SO_2Cl_2 , acts on benzenoid compounds, if at all, uniformly in the remarkable manner first pointed out in the case of phenol by Dubois in 1867 (*Zeit. f. Chemie*, p. 705), and in several other cases by subsequent observers, simply as a chlorinating agent. Sulphuryl chloride is in many respects a remarkable compound: it is very easily produced by the direct union of sulphur dioxide and chlorine in presence of a catalyst, such as camphor, charcoal, or acetic acid, but little heat being evolved in its formation; it is a highly mobile liquid, of low boiling-point, and it is acted on with extreme slowness by water and alkaline solutions. It is, in fact, a surprisingly inert substance possessed of properties by no means such as are usually regarded as characteristic of acid chlorides. The author questions whether, after all, the chlorine in acid chlorides is possessed of special activity. Probably our ideas on the subject are based too much on the consideration of the properties of the most familiar of acid chlorides, acetic or acetyl chloride; benzoic chloride, it is well known, is a far less active substance, and many other acid chlorides are but slowly attacked by water. It would appear that in sulphuryl chloride the chlorine is but loosely held, and that it is easily withdrawn by a compound having an affinity for chlorine—naphthalene, for example. On slightly warming a mixture of this hydrocarbon and sulphuryl chloride, SO_2 is at once evolved, and the naphthalene is rapidly converted into tetrachloride. The SO_2 radicle in the chloride being all but destitute of "residual affinity," the compound has but little tendency to act as a whole. The view that the activity of acid chlorides is conditioned by the oxygen rather than the chlorine is strongly supported by Wagner and Saytzeff's observations, and the later ones of Pawlow (*Annalen*, 188, 104), on the action of zinc organometallic compounds on acid chlorides, which, there can be little doubt, attack the oxygen and not the chlorine:—



Perhaps also the activity even of so powerful an agent as chlorosulphonic acid, SO_3HCl , should be ascribed less to the chlorine than to the oxygenated radicle; this view is borne out by the fact that the analogous compound SO_3EtCl is a very inert substance. Both these compounds act, in the main, as sulphonating agents, and may perhaps be regarded as mere forms of SO_3 . It would almost seem that on very slight provocation they become resolved into SO_3 , and either HCl or EtCl , and that in the case of SO_3HCl the formation of acid chloride (sulphochloride), which is so frequently observed, is effected indirectly by the conjoint action of hydrogen chloride and SO_3 , an interaction taking place analogous to that by which acetic chloride is formed by the conjoint action of hydrogen chloride and phosphoric anhydride on acetic acid.

Pyrosulphuryl chloride, $\text{S}_2\text{O}_5\text{Cl}_2$, which is an extremely active substance, although not rapidly acted on by water, also acts as a chlorinating agent, behaving much as if it consisted of SO_3 and SO_2Cl_2 ; in some cases it gives rise

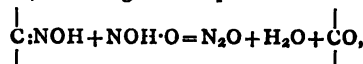
to the formation of a very large proportion of sulphochloride, which probably is a direct product of its action. There is no reason to suppose, however, that even in this chloride the chlorine is specially active.

A detailed description will be given later on of a long series of observations on the action of the various sulphuryl compounds above referred to.

4. "The Action of Nitric Acid on the Ligno-celluloses." By C. F. CROSS and E. J. BEVAN.

Dilute nitric acid attacks the ligno-celluloses when heated with them at 60° . The products are in the first instance a bright yellow derivative of the fibre substance (lignone) and nitrous acid. By the further interaction of these, a characteristic decomposition is determined, large quantities of nitrous oxide (N_2O) being evolved together with carbonic anhydride, only a small proportion of nitric oxide being formed. A sensible quantity of hydrogen cyanide is also produced, the proportion being increased by increase of temperature.

These observations point to the entrance of the NOH residue into the lignone molecule and its interaction with nitrous acid, according to the equation—



the final being the displacement of 2H by O . The action is probably general for compounds containing the NOH residue—hydroximes and nitrolic acids—and the authors suggest that attention should be paid to the gaseous products formed by the interaction of nitric acid and carbon compounds as calculated to elucidate their mechanism.

The investigation, of which this is a preliminary note, is proceeding.

The Chairman, Mr. CROOKES, gave a short verbal account of observations which he had made on the volatilisation of metals *in vacuo* under the influence of an electric discharge.

PHYSICAL SOCIETY.

April 17th, 1891.

Prof. W. E. AYRTON, F.R.S., President, in the chair.

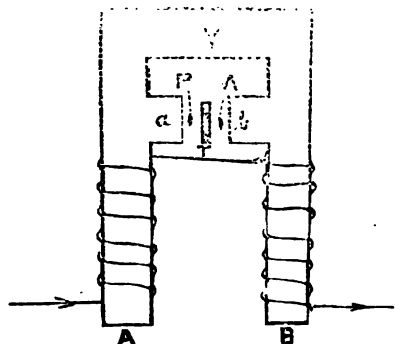
THE following communications were read:—

"On a Property of Magnetic Shunts." By Prof. S. P. THOMPSON, D.Sc.

After referring to a few instances in which magnetic shunts are employed, as, for example, the ordinary magnetic medical coil and Trotter's constant current dynamo, he said that the particular property he wished to speak of was the time taken for such a shunt to lose its magnetism as compared with the other branch of the magnetic circuit. If these times were very different, unsuspected results might be produced, and these might be regarded as being due to a kind of magnetic time-constants. Short pieces, as was well known, demagnetise much more rapidly than long ones, particularly if the latter form, or be part of, a closed magnetic circuit. Hence, in alternators, such as Kingdon's Keeper Dynamo, in which both magnets and armature are stationary, it was important that the revolving keepers should be short. The most important application of a magnetic shunt occurred, he said, in d'Arllincourt's Relay, described in vol. iv. of the *Journal of the Society of Telegraph Engineers and Electricians*, and shown diagrammatically in Fig. 1. In this relay the polarised tongue, τ , plays between two projections, a and b , near the yoke, γ , and it is claimed to have a quicker action than ordinary kinds. The reason of this the author explained as follows:—

When a current flows through the coils, the greater part of the magnetic lines pass through the yoke, but a few leak across from a to b , and move the tongue against the contact, τ . On stopping the current, the magnetism in

extremities A and B dies away much more rapidly than in the yoke; consequently the direction of the field between a and b is reversed, and the tongue, T, thrown back against the stop, Q.



Prof. PERRY asked if any experiments had been made to test whether the throwing back actually occurred. He also enquired whether such action would be augmented or otherwise by having a thick copper tube round the yoke, or by laminating the iron.

Mr. BLAKESLEY asked if placing a yoke across A B would not improve the action.

The PRESIDENT said he would be glad to know whether the relay was any more sensitive than an ordinary one as regards the ampère-turns or the watts required to actuate the instrument. In India he remembered that they use inductive coils shunting the ordinary relays, in order to expedite the action and to avoid confused signals arising from the electrostatic capacity of long lines.

In reply, Prof. THOMPSON said he had tried an experiment on a horse-shoe electromagnet, and found evidence of throwing back when working near the bend or yoke. Putting a yoke across A B would, he thought, tend to neutralise the effect desired.

"An Alternating Current Influence Machine." By JAMES WIMSHURST.

This machine consists of a varnished glass disc, with or without metallic sectors, mounted on an axis, and rotating within a square wooden frame fixed in the plane of the disc. The frame carries four square glass plates, each of which has one corner cut away so as to clear the boss of the disc. These plates are placed one at each corner of the frame, alternately on the two sides, and the disc revolves between them. There are thus two plates on one side of the disc situated at opposite ends of a diagonal of the frame, and two on the other side of the disc at opposite ends of the other diagonal. Tin-foil sectors fixed to the outer sides of the plates act as inductors, and wire brushes connected with them touch the disc about 90° behind the centre of the inductors.

The peculiarity of the machine is that although sparks can be readily obtained from it, a Leyden jar cannot be charged by bringing it to one of the terminals. From this the author concluded that the electricity produced was alternately of positive and negative sign, and this he showed to be the case by means of an electroscope. The alternations, he said, occurred about every $\frac{1}{4}$ of a revolution, the suspended paper disc which he used as electroscope remaining apart for that period and collapsing during the next quarter of a turn.

Using discs with various numbers and sizes of sectors, the author finds that the smaller the sector and the fewer the number, the greater the quantity of electricity produced. Plain varnished glass is the best in this respect. Such a disc, however, does not excite itself quite so freely as one having numerous metallic sectors.

By removing two of the inductors and placing an insulating rod carrying collecting brushes at its ends

across a diameter of the disc, the machine was used to produce direct currents. Numerous discs and various shaped inductors accompanied the machine, by means of which a Holtz, Voss, or ordinary influence machine could be imitated.

Prof. S. P. THOMPSON congratulated the author on the most interesting and puzzling machine he had brought before the Society. He enquired if the machine would work if the direction of the rotation was reversed, or if two of the inductors were removed, and also whether all the four inductors are electrically of the same sign at the same instant.

In reply, Mr. WIMSHURST said the machine would not excite if the direction of rotation be changed without also changing the direction of the brush arms, but it would work as a direct current machine when two inductors were removed.

"On Erecting Prisms for the Optical Lantern, and on a New Form of Erecting Prism made by Mr. Ahrens." By Prof. S. P. THOMPSON, D.Sc.

The ordinary form of erecting prism, viz., a right-angled isosceles one, was, the author pointed out, open to the objection that the top halves of the faces enclosing the right angle were nearly useless, for only the light which after the first refraction is totally reflected by the hypotenuse face can be utilised. The fraction of the side which is useful varies with the refractive index, being 0.46 when $\mu=1.5$, and 0.525 when $\mu=1.65$. To increase these proportions, prisms with angles of 105° and 126° have been used by Wright and others, and in some cases the prisms have been truncated. With such large angles, much light is lost by reflection. Bertin employed two truncated right-angled prisms placed base to base with an air film between them. Nachet has also made erecting prisms for microscopes, in which internal reflections occur from faces inclined at an angle of 81° to each other. This form of prism suggested to Mr. Ahrens the new form now shown, and which may be described as a long right-angled prism whose ends are cut off so as to be parallel to each other and inclined at 45° to the hypotenuse face. The longitudinal acute angles, not being required, are truncated.

Light falling parallel to the axis on one end of the prism is refracted, and after internal reflections emerges parallel but perverted.

It is claimed that this form of prism gives, weight for weight, a larger angular field than any previously made.

The performance of the new form of prism and also of the ordinary form was tested before the Society.

At the close of the meeting, Dr. Atkinson, who had previously taken the chair, announced that the next meeting would be held at Cambridge on May 9th, instead of May 8th as previously intended.

NOTICES OF BOOKS.

A System of Inorganic Chemistry. By WILLIAM RAMSAY, Ph.D., F.R.S., Professor of Chemistry in University College, London. London: J. and A. Churchill (8vo., pp. 700).

WITH the exception of bulky works of reference, such as those of Watts and of Roscoe and Schorlemmer, it is rare to meet with a systematic treatise on chemistry which can be examined without weariness. We have generally to exclaim: "all this is no doubt quite accurate, but it has already been written, with unimportant verbal modifications, over and over again. Wherefore *cui bono*?" The present work forms a happy exception. In size it is a useful medium between the encyclopædic treatises above referred to, and the bald manuals and manualettes admittedly written to meet the requirements of this or that syllabus. Professor Ramsay

writes to teach chemical sciences, not to aid in that unhappy "sacrifice of education to examination," which is still going on as grimly and as ruinously as ever.

He bases his work on the periodic classification of the elements, which, long as it has been in our hands, has been neglected by the routine teachers of chemistry. He ignores the absolute boundary line between the metals and the non-metals, or "metalloids," as France still persists in calling them. He protests against the undue importance still allotted to the supposed antithesis between the acid and the basic hydroxides, and regrets that our text-books, whilst professing to teach *pure* chemistry, have still been too much swayed by commercial considerations. Why, indeed, should the notions of rarity or abundance, of utility or uselessness, be regarded at all in a scientific work. Such considerations we must hand over to works on technical and industrial chemistry, where they are all-important. It is scarcely necessary to add that none of the elements are omitted. The rare earths are most ably discussed in a separate chapter in conjunction with spectrum analysis, which has played so important a part in their discovery and study. We are exceedingly glad to find this important method of research receiving here an attention which contrasts happily with the perfunctory notice which it meets with in books not a few.

The arrangement adopted in the work is first to take the elements in their periodic order, next their halogen compounds, single and double, the oxides, sulphides, selenides, and tellurides following next. The borides, carbides, and silicides, the nitrides, phosphides, arsenides, and antimonides succeed, along with the organo-metallic compounds, the double ammonia compounds, and the cyanides.

Manufacturing processes are transferred to the end of the work, those substances which are usually made in the same class of establishments being treated together. The chemical principles involved are brought into prominence rather than the details of the plant.

After a careful examination we must declare ourselves well satisfied with this work. We consider it especially adapted for that numerous class of readers who need something superior to the current cram-books, but who yet have not time to devote to such works as that of Roscoe and Schorlemmer.

Intensity Coils: How Made and How Used. By "DYER."

With a Description of the Electric Light, Electric Bells, Electric Motors, the Telephone, the Microphone, and the Phonograph. Sixteenth Edition. London: Perken, Son, and Rayment.

This work must have met a public want, as we see at once from the fact of its having reached its sixteenth edition. Some of the matter which is added scarcely falls within the original scope of the work, though it may attract public attention at present. The author describes, with the necessary illustrations, a number of experiments calculated to explain the construction, properties, and uses of the battery, and of the Ruhmkorff coil. This important instrument of research is figured three times, on pp. 5, 28, and 38. We are not quite sure whether here or in other departments of physical science the amateur will derive much advantage from making or attempting to make his own apparatus.

Supposing him completely successful it will still have been at the cost of a great outlay of time which might have been better employed. The experiments are, generally speaking, described with correctness, and the work will doubtless be of advantage to persons who wish to acquire a practical knowledge of the rudiments of electric science.

As regards the final chapter, "seeing by electricity," we must not forget that the question can scarcely be considered within the bounds of possibility. That its importance, if really effected, would be almost infinitely

greater than that of all the devices for transmitting sound is undeniable.

A Treatise on Chemistry. By Sir H. E. Roscoe, F.R.S. and C. SCHORLEMMER, F.R.S. Volume III. *The Chemistry of the Hydrocarbons and their Derivatives or Organic Chemistry.* Part III. New and thoroughly revised Edition. London and New York: Macmillan and Co.

THE volume before us discusses that most important series of bodies known as the aromatic compounds, which indeed have increased so rapidly in numbers that the authors are justified in speaking of "Aromatic Chemistry." It has been found necessary to re-cast the present edition of the work to a very great extent. The rapid flow of discovery involves not merely additions to what is already known, but very often important modifications. Hence the task of keeping fully abreast of the present position of the science is most arduous, and the credit due to the authors for the manner in which they are executing their undertaking is correspondingly high.

After an introduction the authors describe benzene, hydroxybenzene, and its allies, its amido-derivatives, its diazo-hydrazine and azo-derivatives, including the azo-dyes, the thio-amido compounds, and the phosphorus, arsenic, antimony, bismuth, boron, silicon, tin, lead, and mercury derivatives of benzene.

As a systematic treatise on chemistry, the work taken in its entirety has no equal in the English language.

Examen Químico y Bacteriológico de las Aguas Portables.

Par A. E. SALAZAR y C. NEWMAN. Con un Capítulo del Dr. Rafael Blanchard sobre los Animales Parásitos introducidos por el Agua en el Organismo. ("Chemical and Bacteriological Examination of Potable Waters," by A. E. Salazar and C. Newman; with a Chapter by Dr. R. Blanchard on Parasitic Animals, introduced into the Organism by Water). London: Burns and Oates.

THE present work is a step in a direction very much needed. Spain and her former magnificent colonies in America have not been precipitate in sanitary reforms, and it is therefore very pleasing to welcome a volume on this subject, which, if published in London, has been written in Chili, and is based upon researches conducted in the laboratory of the Naval School of Valparaíso.

The authors have taken up their subject in a comprehensive manner, treating successively of the search for mineral impurities, for organic pollutions, and for microbia.

They consider that a good potable water should contain 0.30 grm. of useful saline elements per litre. They suggest that bright, hard waters are likely to contain less organic impurity than such as are soft. They admit, however, that waters containing much magnesia, especially in the state of nitrates, have a debilitating action. The presence of copper they regard as less formidable than that of lead.

As noxious salts they class those of iron, lead, and copper. Now iron salts are certainly very objectionable in technical operations, but they may be pronounced harmless to the human system in any proportion in which they are likely to occur in potable waters. Instructions are given for the detection of arsenic, barium, and zinc, but chrome is overlooked—an impurity which sometimes finds its way into the waters of industrial districts.

For the determination of the organic impurities the authors give in full the processes of Wanklyn, Chapman, and Smith, and three modifications of the permanganate process, that with alkaline permanganate and ferrous sulphate, that with alkaline permanganate and oxalic acid, and that with acid permanganate and oxalic acid.

The remainder of the work is devoted to an account of the methods for detecting bacteria, taking the term in its widest sense. The authors lay great weight upon such

researches, but they insist upon the necessity for experimental infection as the means of verifying the results obtained. This method is at present open to sanitary experts in Chile; but as that country has succeeded in naturalising cholera it may sometime be visited by an epidemic of "zoophily."

The work is illustrated with 127 engravings, sixteen micro-photographs, and five photographs of cultivations. It will be found a most valuable contribution to sanitary science wherever the Spanish language is spoken.

Die Elektrischen Verbrauch's Messer. ("Measuring Instruments for the Consumption of Electricity.") By ETIENNE DE FODER. Vienna, Port, Leipzig: Hartleben (small 8vo., pp. 219).

This work forms the 43rd volume of the "Electro-technical Library" (*Elektrotechnische Bibliothek*), issued by the well-known publisher whose name it bears. It appears that almost all the operations of the electric current have been pressed into the important service of measuring its quantity. Thus we have electro-chemical, electro-motive, galvanometric (so-called), electro-thermic, and electro-capillary measuring instruments. More than eighty such appliances are described in the work before us, though many others are admittedly left out of consideration. As units of consumption there are described the Edison lamp-hour, the Ampère-hour, and the Watt-hour.

The properties which an electrical measuring instrument must possess are enumerated, as accuracy, capacity—i.e., adaptability to currents of great and small strength—minimum waste of energy, simplicity—a point in which most instruments are sadly deficient—durability, care, registration of results, an object which is far from having been attained. The author in discussing this point goes out of his way to defend the accuracy of gas-meters, an utterly untenable position in the face of demonstrated facts.

Another property required from a good instrument is that it should admit of ready verification. A very important condition is that the instrument should not admit of fraudulent interference.

The author divides the instruments into the following classes: electro-chemical meters without self-registering mechanism depending on the laws of electrolysis; similar instruments with a registering mechanism; electro-chemical meters with a movable or reversible electrode; gas-expansion meters depending on the volt-metre; electro-mechanical meters; electro-motive meters in which the current effects the rotation of a motor; alternating current meters on the electro-motive principle; ampère or coulomb meters, in which the vibrations of the needle of an ammeter are registered by clockwork; mercurial rotation meters, electro-thermic meters; photographic meters; meters depending on Foucault's disc; meters worked by accumulators; meters with electro-dynamometers; and lamp-hour or consumption meters. The author then proceeds to an account of the most successful of these instruments, descriptions being made more intelligible by means of seventy-seven well executed illustrations.

This work must be pronounced exceedingly useful, though it is, perhaps, written too much in the interests of the supplier, who it is to be hoped will act more uprightly than gas companies have generally done.

An appendix gives an account of the conditions under which electric current is supplied in various cities whether for lighting or as a source of motive power.

Examination of Horse-Hair.—M. Goeldner (*Pharm. Zeit.*).—The presence of oil is detected by pressure between silk-paper. Vegetable fibre is recognised by its different behaviour on burning, and by its resisting prolonged treatment (12 hours) with dilute soda-lye (1:5).

CORRESPONDENCE.

A GERMAN ACCOUNT OF JOSEPH PRIESTLEY.

To the Editor of the Chemical News.

SIR,—In the *CHEMICAL NEWS* (vol. lxii., p. 84), I pointed out some singular mis-statements by French authors concerning the biography of the discoverer of oxygen.* Though I lay no claim to be a champion of Priestley in particular, I do like to have justice done, and I love truth; allow me, therefore, to use your columns to direct attention to a brief biography of Priestley, recently published in Germany, that contains an amazing number of gross mis-statements and makes important omissions.

Dr. Carl Schaedler in his "Biographisch-literarisches Handwörterbuch der wissenschaftlich bedeutenden Chemiker" (Berlin 1891), writes of Dr. Priestley thus:—"Im Jahre 1761 war er Sprachlehrer an der Academie zu Warrington nachdem er die verschiedensten Länder Holland, Frankreich, Italien, Deutschland bereist hatte. In diesen Ländern machte er, nicht vorbereitet durch ein eigentliches naturwissenschaftliches Studium, seine glänzenden Untersuchungen," [&c.].

The facts are as follows:—Priestley did not make his journey on the Continent with Lord Shelburne until the summer of 1774, and he visited, as he himself wrote, "Flanders, Holland, and Germany as far as Strasburgh," and spent one month in Paris. Priestley never visited Italy, but it is not this trifling inaccuracy nor the error of thirteen years for the date of his travels of which I would complain; I earnestly protest against Schaedler's ingenious attempt to transfer the scene of Priestley's memorable chemical discoveries to the Continent; "*In diesen Ländern*," forsooth, "*machte er*" his investigations on different kinds of airs.

After quoting Priestley's own account of his discovery of oxygen Dr. Schaedler writes:—"Priestley ist mit van Helmont Begründer der pneumatischen Chemie," an association tending to belittle the Englishman's renown.

Again we read:—"Die Unduldsamkeit in religiösen Dingen entzweite Priestley mit seinem Gönner Lord Shelburne (*sic*), er verarmte und wanderte 1794 nach America aus, liess sich an den Quellen des Susquehanna als Farmer nieder und wurde 1804 vergiftet."

To anyone familiar with the life of Priestley, this sentence combines an amazing number of mis-statements; Priestley himself wrote he never knew the exact cause of the coolness that arose between himself and Lord Shelburne. In place of a reference to the unhappy Birmingham Riots of 1791, we are told that "er verarmte"; and finally a statement so baselessly persisted in by the French writers, that Priestley died by poison, completes this parody of a biography.

Such blunders are inexcusable because accurate information as to Priestley's life is accessible to every one; he left autobiographical "Memoirs" that furnish data for the innumerable biographies published in dictionaries and encyclopedias of every nation during nearly one hundred years.

Dr. Schaedler's volume shows other signs of careless compilation; the discovery of bromine is ascribed to "Ballard," this is perhaps a mere typographical slip. The author states that Kunckel prepared phosphorus from bones in 1678, whereas every tyro knows that nearly one hundred years elapsed between the preparation of the element from urine and its discovery in bones by Gahn, or Scheele (1769).

Dr. Schaedler's little work does not claim completeness, but it is difficult to understand on what principle he selects the "wissenschaftlich bedeutenden Chemiker," whom he honours. He does not even include all the honorary members of the German Chemical Society, omitting the names of Dr. Warren de la Rue, F.R.S., Dr.

* French Accounts of Joseph Priestley," *CHEMICAL NEWS*, lxi., 84.

W. H. Perkin, F.R.S., and Dr. Wolcott Gibbs (the latter of the U.S.A.).

Of Frenchmen eminent in Chemistry we miss the names of Lecoq de Boisbaudran, Friedel, Grimaux, Moissan, and others. Americans fare badly, but four being named. Can it be that the author is not acquainted with the researches of such men as Robert Hare, Professor Frederick A. Genth, Professor T. Sterry Hunt, Dr. J. Lawrence Smith, Professor J. W. Mallet, F.R.S., Prof. Josiah P. Cooke, and a host of others whose scientific labours entitle them to high places in the annals of chemistry. Their biographies and writings are found in the late Professor Silliman's "American Contributions to Chemistry," presented in 1874 at the Northumberland celebration of the centennial of the discovery of oxygen.

Dr. Schaedler's work is very unequal in its bibliography—a title more in accordance with its contents would be:—"Handwörterbuch *einige in Deutschland wissenschaftlich-bedeutenden Chemiker.*"—I am, &c.,

H. C. B.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Justus Liebig's Annalen der Chemie.
Vol. cliv., Parts 1 and 2.

Researches from the Chemical Institute of the University of Strasburg.—These communications consist of memoirs by R. Fittig on lactic acids, lactones, and non-saturated acids, commencing with the synthesis of lactic acids by the condensation of aldehydes with bibasic acids and their behaviour on dry distillation; by Ignaz Fraenkel on acetaldehyd and succinic acid; by H. East Miller on chloral and succinic acid; by Alf. Delisle on propionic aldehyd and succinic acid; by Alb. Schmidt on butyric aldehyd and succinic acid; by Adolf Zauner on isobutyraldehyd and succinic acid; by August Schneegans on valeraldehyd and succinic acid; by Franz Feist on valeraldehyd and pyrotartaric acid; by an anonymous chemist on cœnanthol and succinic acid; by R. Reichelmann on cœnanthol and pyrotartaric acid, and by R. Fittig on benzaldehyd and succinic acid.

Communications from the Chemical Laboratory of the University of Erlangen.—These consist of memoirs by O. Fischer and E. Hepp on para-nitroso-diphenyl-meta-phenyldiamine; by A. Harden on β -nitroso α -naphthylamine; by A. Reichold on phenyl-paratolylamine; by L. Pflug on paraxylidine; by Th. T. Best on monomethyl-ortho-anisidine; and by C. Heucke on para-amido-diphenylamine.

Researches from the Agricultural Chemical Laboratory of the University of Göttingen; consisting of papers by Dr. K. Beythien and B. Tollens on the compounds of raffinose with bases; by the same authors on the behaviour of inverted raffinose with phenylhydrazine; by the same authors on the melting-points of the osazones, and on researches with phenylhydrazine; and by Dr. K. Beythien, Dr. E. Parcus, and B. Tollens, on the formation of lactic acid from raffinose, and from cane-sugar with bases, the conclusion being that raffinose cannot be formed from cane-sugar by the action of lime or strontia, and by the same authors on lactic acid from treacle. The quantity of lactic acid present in (beetroot) treacle may reach $\frac{1}{4}$ per cent. For its formation a double weight, or upwards, of sugar must have been decomposed.

Compounds of Alloxan with the Pyrazol bases.—By Guido Pellizzari.—Alloxan, although it has acid

functions, behaves with bases quite differently from the other acetones and aldehyds. In consequence of the instability of the alloxan chain this reaction may serve for the preparation of bodies which are not easily obtained in any other manner. Skatol and phenylpyrazol do not combine with alloxan. Methylketol forms a saline compound which is again resolved into its two constituents by alkalies and acids. Anilalloxan, if heated with acids, gives off carbonic acid, ammonia, and formic acid, and yields the salt of an aminic acid.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

India-Rubber.—A correspondent asks if any one can tell him of a chemical which will keep raw india-rubber pulp in a plastic state of the consistency of china-clay or dough. Raw india-rubber pulp is of a stringy, plastic nature, and the object is to reduce the stringiness and make it of shorter consistency, like dough or china-clay. The substance added must not injure the rubber and must be capable of being expelled by boiling or at a similar heat after it has done its service.

MEETINGS FOR THE WEEK.

- MONDAY, 4th.—Medical, 8.30. (Annual Oration).
— Society of Arts, 8. "The Decorative Treatment of Natural Foliage," by Hugh Stannus, F.R.I.B.A.
— Society of Chemical Industry, 8. "An Improved Process for Softening and Clarifying Water," by Mr. L. Archbutt and Mr. R. M. Deeley. "The Chemistry of Whisky and Allied Products," by Mr. A. H. Allen.
— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 5th.—Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Royal Institution, 3. "Bacteria: their Nature and Functions," by Edward E. Klein.
— Society of Arts, 5. "Armenia and the Armenians," by Capt. Buchan Telfer, R.N.
WEDNESDAY, 6th.—Society of Arts, 8. "The Sources and Applications of Borax," by Mr. E. L. Fleming.
— Geological, 8.
THURSDAY, 7th.—Royal Institution, 3. "Recent Spectroscopic Investigations," by Prof. Dewar, M.A., F.R.S.
— Institute of Electrical Engineers, 8.
— Chemical, 8. Ballot for the Election of Fellows.
"The Action of Alkalies on the Nitro-compounds of the Paraffin Series," by Prof. Dastan and T. S. Dymond. "The Addition of the Elements of Alcohol to the Ethereal Salts of Unsaturated Acids," by Prof. Purdie and W. Marshall. "On some New Addition Compounds of Thiocarbamide affording Evidence of its Constitution," by Prof. Emerson Reynolds. "On the Action of Acetic Anhydride on Substituted Thiocarbamides, and an Improved Method of Preparing Aromatic Mustard Oils."
FRIDAY, 8th.—Royal Institution, 9. "Liquids and Gases," by Prof. W. Ramsay, F.R.S.
— Physical, 5.
SATURDAY, 9th.—Royal Institution, 3. "The Artificial Production of Cold," by H. Graham Harris, M.Inst.C.E.

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THE CHEMICAL NEWS.

VOL. LXIII., No. 1641.

A SYSTEM OF INTERNATIONAL MEASURE AND WEIGHT.

By C. J. HANSEN, Civil Engineer.

To the great nations who, entirely or partly, use the British standards of measure and weight, and for reasons of practical utility and convenience hesitate to adopt the metric system, the author most respectfully offers a system of decimal measure and weight, based upon the present Anglo-American system, which, by only a minute increase in the length of the foot, is converted into a decimal system of measure and weight, combining the convenience of the present Anglo-American standards, with all the scientific and theoretical advantages of the metric system, viz., a simple relation between the unit of length (which determines volume), the unit of mass, and the unit of specific gravity.

In case England adopts this system, no doubt the United States and Russia would follow, and it would finally become the world's standard.

The author's new system is simply this:—

The foot is increased by about $\frac{1}{32}$ of its present length, or the thickness of ordinary note-paper,—(exactly from 1'0000 to 1'000403), while the pound avoirdupois, the ounce, and the imperial gallon remain unaltered. By this very slight alteration of the length of the foot, which hardly will be noticed in trade, manufacture, and commerce, the present system of standards is at once converted into a decimal system. While the present cubic foot only contains 436971.78 grains of distilled water, the new standard cubic foot would contain exactly 1000 ounces (437,500 grains) of distilled water of 4° C. temperature*; 16 cubic feet consequently will be equal to 100 gallons (called 1 hectogallon), and 1 hectogallon of distilled water of 4° C. weighs 1000 lbs. The new standard foot will be divided into deci-, centi-, and milli-foot, and by multiplying the foot we get:—

Surveyors and Nautical Measure.

Length.		
1 rod	= 5 ft.	= 10 links.
1 chain	= 10 rods	= 100 "
1 mile	= 100 chains	= 10,000 "

Square.		
1 sq. rod	= 100 sq. links.	
1 sq. chain	= 10,000 "	
1 sq. mile	= 10,000 sq. chains.	

Cube.		
1 cube rod	= 1000 cube links.	
1 " chain	= 1000 " rods.	
1 " mile	= 1000'000 " chains.	

1 knot or nautical mile ($\frac{1}{60}$ ° latitude) = 6080'22 ft. (The Admiralty knot is now 6080 ft.).

Fluid and Dry Measure.

(The imperial gallon remains unaltered).

	Lbs. of distilled water at 4° C.		
1 hectogallon	= 100	gallons = 1000	= 16 cubic feet.
1 gallon	= 0'01 hgal.	= 10	" "
1 dion (decigal.)	= 0'1	gallon = 1	" "
1 centigallon	= 0'01	" = 0'1	" "
1 milligallon	= 0'001	" = 0'01	" "

* At 4° C. water has its point of greatest density, and this temperature also is adopted in the metric system.

Weights.

The pound avoirdupois, and the ounce remain unaltered.

Distilled water.

1000 lbs. = 1 hgal. = 1 kilopound = $\frac{1}{16}$ new ton.
1000 ozs. = 1 cubic ft. = 1 kilounce = $\frac{1}{16}$ kilopound.

The pound is divided into deci-, centi-, and millipounds.

The ounce is divided into deci-, centi-, and milliounces.

Trade and Commercial Standards.

The new standard foot divided into 12 inches, &c., may be used where convenient. The ton reduced to 2000 lbs. and the cwt. of 100 lbs. to be legalised.

Terms and Units Based upon the New Decimal Standards.

Specific Gravity.—The weight of one cubic deci-foot of a substance in ounces, or the weight of a dion (decigallon) of a substance in pounds, expresses the specific gravity of the substance. Quotations of specific gravity could be made perfectly international if they were referred to the 42° latitude and sea level. Mean atmospheric pressure at that latitude is 759'72353 m.m. of mercury (760 m.m. is commonly reckoned as mean atmospheric pressure), and under this pressure the specific gravity of oxygen gas is $\frac{1}{16}$ of the weight of distilled water, or:—

1 hectogallon oxygen gas of 0° C. weighs exactly $\frac{1}{16}$ lbs., and 1 lb. of oxygen contains exactly $\frac{1}{16}$ hectogallon; the specific gravity of any other aeriform substance is found with absolute accuracy by multiplication with the substances atomic number, and these figures also hold good for metric standards.

1 hectogallon weighs .. lbs.	1 lb. contains hectogallons.
1 cubic foot .. ozs.	1 ounce .. cubic feet.
1 cubic metre .. klgr.	1 kilogr. .. cub. metres.
Hydrogen .. $\frac{1}{16}$	Hydrogen .. $\frac{1}{16}$
Oxygen .. $\frac{1}{8}$ (16 x $\frac{1}{16}$)	Oxygen .. $\frac{1}{8}$
Carbon vapour (12 x $\frac{1}{16}$)	Carbon vapour .. $\frac{3}{8}$
Carbonic oxide (14 x $\frac{1}{16}$)	Carbonic oxide .. $\frac{7}{8}$, &c.

The specific heats of gases are found and expressed in equally plain manner, and all calculation relating to aeriform substances are thereby immensely simplified.

Unit of Heat.—1 lb. of water heated 1° C. called one calor.

The centigrade thermometer must be adopted, and its boiling-point lowered $\frac{1}{4000}$ th in accordance with the international barometric standard.

Atmospheric pressure is usually measured by inches or m.m. of mercury, but if atmospheric pressure at 42° latitude were adopted as the universal mean atmospheric pressure, and this unit divided into 1000 or 10,000 parts, we should have a far more convenient measure and expression of the pressure of the atmosphere for steam, gases, or fluids, than the present inches of mercury or pounds per sq. in.

The readings of the barometer would be 0'947—1'000—1'012, &c. (atmosphere).

72 lbs. per sq. in., steam pressure in a boiler would be expressed: 4'91 atmosphere.

Pressure in a gas-pipe, say 0'6 inch head of water = 15 (ten thousands), &c.

Numerous problems, especially in steam and gas engineering, dynamic, thermo-dynamical, and thermo-chemical science (which now are a task for eminent engineers and professors), become, by the introduction of the new decimal standards and the international standard of gravity, so extremely simple that practical men of ordinary capacity and even clever schoolboys are able to understand and to solve them.

* See the discussion in the Institution of Mechanical Engineers, July, 1889, on Mr. Macfarlane Gray's paper, "The Rationalisation of Regnault's Experiments on Steam."

The system fully worked out and its applications are nearly ready for the press.

The author respectfully solicits thorough discussion of this system.

Copenhagen, 3, Valdemarsgade, V.,
April, 1891.

EIGHTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

THE Committee reports the publication of the following works:—

1. "Index to the Literature of the Butines and their Halogen Addition Products" (1863—1887). By Mr. Arthur A. Noyes, in the *Technological Quarterly*, Boston, for December, 1888.

This should have been noticed earlier, but owing to the absence of the author, now in Europe, it was overlooked. It comprises an author- and a subject-index; the abbreviations used are those of the Standard List prepared by this committee.

2. "Index to the Literature of Thermodynamics." By Dr. Alfred Tuckerman. Miscellaneous Collections of the Smithsonian Institution, No. 741. Washington, D.C., 1890, pp. vi.—239.

This contains an author-index and a subject-index.

3. "Index to the Literature of Amalgams." By Prof. Wm. L. Dudley. In his Vice-Presidential Address to the Amer. Assoc. Adv. Science at Toronto.—*Proc. Amer. Assoc. Adv. Science* for 1889, pp. 161—171, 1890, 8vo.

4. "A Bibliography of Analytical Chemistry for 1883."—*Journ. Anal. Chem.*, iii., 1889.

5. The same for 1889.—*Journ. Anal. Chem.*, iv., 1890; and,

6. "A Bibliography of Chemistry for the Year 1886." Smithsonian Report for 1886—87. Washington, 1889.

These brief bibliographies are by Dr. H. C. Bolton.

7. Professor A. A. Breneman, in a "Historical Summary to his Memoir on the Fixation of Atmospheric Nitrogen" (*Journ. Amer. Chem. Soc.*, xi.), gives many bibliographical data.

The "Index Pharmaceuticus," published in the *Pharmaceutical Era* (monthly), and noticed in our sixth annual report, grows in scope and value. It is an alphabetical subject-list of original papers and important reprints and abstracts, appearing in thirty-two periodicals, English, American, French, and German. Although pharmacy is dominant, chemical topics are often included. The subject-index is followed by an author-index referring to the former.

The committee further report that several volunteer indexers are making progress. Dr. Alfred Tuckerman is engaged on an Index to the Chemical Influence of Light, and is planning more work of great value. Dr. James Lewis Howe is indexing the metals of the platinum group. Dr. H. C. Bolton reports progress on a Select Bibliography of Chemistry, which is an extension of the Bibliography of Historical Chemistry previously noticed; in the enlarged plan he is being assisted by Dr. Alfred Tuckerman.

As often stated in these annual reports, the Committee limits its duties to the encouragement of volunteer-indexers and to chronicling work performed. The fact that undertakings announced several years ago have not been recently noticed does not always indicate their abandonment; many will undoubtedly be brought to completion by their authors. Many chemists who are willing to contribute their quota to the general scheme are, however, deterred from making definite offers by the in-

adequacy of the libraries to which they have convenient access. This difficulty is a real one, and suggests that much might be accomplished by co-operation of several persons in a single subject, each indexing the sets of periodicals available, and submitting the partial work to one of the number for editing. In such an enterprise, conference between the several chemists uniting on a given topic would be necessary to avoid duplication and to secure a uniform plan.

Prof. W. O. Atwater, Director of the Office of Experiment Stations, Department of Agriculture, Washington, D.C., in conference with the committee, calls attention to the desirability of securing bibliographies and indexes to certain topics in the chemistry of plants and animals, such as (1) chemistry of albumenoid compounds; (2) chemistry of the so-called amid-compounds and kindred bodies; (3) chemistry of the fatty bodies; (4) chemistry of the lecithins, waxes, chlorophylls, chloresterin, &c.; (5) chemistry of the carbohydrates. These to meet a need which is being more and more keenly felt by physiological and agricultural chemists.

Subsequent to the presentation of this report, the Chemical Section authorized the insertion of the following minute:—

After a discussion in the Section on the continuance of a committee to confer with others with a view to founding a National Chemical Society, Dr. Albert B. Prescott suggested as a proper function of such a society the publication of an index to periodical chemical literature. He deprecated the multiplication of periodicals, and maintained the utility and importance of an index to the contents of those already in existence.

Respectfully submitted,

H. CARRINGTON BOLTON, *Chairman*.

F. W. CLARKE.

ALBERT R. LEEDS.

ALEXIS A. JULIEN.

JOHN W. LANGLEY (in Europe).

ALBERT B. PRESCOTT.

CONCERNING THE PENTAGLUPOSES.*

By W. E. STONE.

(Concluded from p. 207).

B.—Quantitative Reduction of Fehling's Solution by the Pentagluposes.

BOTH arabinose and xylose reduce Fehling's solution strongly, but their quantitative relation to it has not previously been studied, with the exception of a brief mention by Bauer of some limited determinations for arabinose, from which he concluded that it possessed in a slight degree greater reducing power than dextrose (*Landwirtschaftliche Versuch-Stationen*, xxxvi., 304).

In view of the common occurrence of the pentagluposes, as already pointed out, it is evident that in the quantitative examination of any material for carbohydrates by hydrolytic methods, i.e., by inversion with acids and titration of the glucose thus formed with Fehling's solution, we may be dealing not only with the true glucoses derived from starch, cane sugar, &c., but also with more or less of one or both of the pentagluposes, since we know that the gums from which the latter are derived easily undergo hydrolytic change by the action of acids. Such analytical results may, therefore, be erroneous from two causes: first, from the assumption that the reduction of Fehling's solution is due solely to the presence of the true glucoses; or, second, from the assumption that the pentagluposes, when present, reduce Fehling's solution in the same degree as the true glucoses.

Take, for example, such a material as brewers' grains,

* From advance proofs of the "Proceedings of the American Association for the Advancement of Science," vol. xxix. Communicated by H. Carrington Bolton.

* Contributions from the Chemical Laboratory of Purdue University. From the *American Chemical Journal*, Vol. xiii., No. 2.

in which it might be desired to ascertain the thoroughness of malting and fermentation by determining the residual carbohydrate. Such material might contain no trace of starch or sugar, and yet might give abundant indications of the presence of these substances after inversion, because it contains so large an amount of the pentaglucoose bodies that it is possible to isolate from it 2 per cent, or more, of the crystallised pentaglucooses (*Liebig's Ann. Chem.,* 241).

It seemed important, therefore, to know the relations existing between these bodies and the true glucoses, and I therefore determined the comparative values of arabinose and dextrose in dilute solutions toward Fehling's solution.

1. *Arabinose*.—The material used was prepared by me from cherry gum, and was pure, as was shown by its specific rotation ($[\alpha]_D = 104.1^\circ$). From this material, solutions of 1, $\frac{1}{2}$, and $\frac{1}{4}$ per cent strength were made. The Fehling's solution was prepared according to the standard formula, viz., 34.639 grms. of hydrous copper sulphate dissolved to a volume of 500 c.c., and 60 grms. sodium hydrate with 173 grms. sodium potassium tartrate dissolved to a volume of 500 c.c., the two solutions being preserved separately, and mixed in equal volumes just before using. The determinations were made gravimetrically as follows:—

70 c.c. of the Fehling's solution were brought to boiling, and exactly 25 c.c. of the arabinose solution quickly run in from a full pipette, after which the whole was kept over the flame exactly four minutes, of which the first fifty to sixty seconds were consumed in bringing the liquid to boiling again. The time of boiling and filtering was observed carefully. The precipitated cuprous oxide was collected on a Soxhlet asbestos filter with the aid of a pump, washed with boiling water, alcohol, and ether, reduced to metallic copper in a current of dry hydrogen over a low flame, and, after cooling in hydrogen, weighed. The following are the results obtained:—

$\frac{1}{4}$ per cent Solution.—25 c.c., containing 0.250 gm. arabinose, precipitated respectively:—

1. 0.4850 gm. copper.
2. 0.4874 "
3. 0.4860 "

An average of 0.48623 gm. copper, or for 0.001 gm. arabinose 0.001945 gm. copper.

$\frac{1}{2}$ per cent Solution.—25 c.c., containing 0.1875 gm. arabinose, precipitated respectively:—

1. 0.3621 gm. copper.
2. 0.3631 "
3. 0.3640 "

An average of 0.36187 gm. copper, or for 0.001 gm. arabinose 0.001929 gm. copper.

$\frac{1}{4}$ per cent Solution.—25 c.c., containing 0.125 gm. arabinose, precipitated respectively:—

1. 0.2446 gm. copper.
2. 0.2430 "
3. 0.2479 "

An average of 0.2448 gm. copper, or for 0.001 gm. arabinose 0.001958 gm. copper.

$\frac{1}{2}$ per cent Solution.—25 c.c., containing 0.0625 gm. of arabinose, precipitated respectively:—

1. 0.1264 gm. copper.
2. 0.1248 "
3. 0.1250 "

An average of 0.1254 gm. copper, or for 0.001 gm. arabinose 0.002 gm. copper.

From this it appears that in solutions of 1 per cent, or less, strength, 1 m.grm. of arabinose precipitates 1.9—2 m.grms. of copper.

2. *Xylose*.—The material used was prepared from wheat straw, and was of the desired purity, as shown by its

specific rotation ($[\alpha]_D = 18.41^\circ$).^{*} The determinations were made under conditions as nearly as possible identical with those for arabinose, with the following results:—

1 per cent Solution.—25 c.c., containing 0.250 gm. xylose, precipitated respectively:—

1. 0.4686 gm. copper.
2. 0.4640 "
3. 0.4667 "

An average of 0.4664 gm. copper, or for 0.001 gm. xylose 0.001864 gm. copper.

$\frac{1}{2}$ per cent Solution.—25 c.c., containing 0.1875 gm. xylose, precipitated respectively:—

1. 0.3444 gm. copper.
2. 0.3446 "
3. 0.3462 "

An average of 0.3451 gm. copper, or for 0.001 gm. xylose 0.001841 gm. copper.

$\frac{1}{4}$ per cent solution.—25 c.c., containing 0.125 gm. xylose, precipitated respectively:—

1. 0.2378 gm. copper.
2. 0.2366 "
3. 0.2381 "

An average of 0.2375 gm. copper, or for 0.001 gm. xylose 0.0019 gm. copper.

$\frac{1}{2}$ per cent solution.—25 c.c., containing 0.0625 gm. xylose, precipitated respectively:—

1. 0.1235 gm. copper.
2. 0.1222 "
3. 0.1217 "

An average of 0.1224 gm. copper, or for 0.001 gm. xylose 0.001959 gm. copper.

Under the stated conditions, therefore, 1 m.grm. of xylose precipitates 1.86—1.959 m.grms. of copper.

Dextrose, the most strongly reducing glucose heretofore studied, precipitates, under similar conditions, 1.8—1.9 m.grms. copper, or slightly less than the pentaglucooses. Stated in another way, the amounts of the different sugars in 1 per cent solution required to precipitate the entire copper from 1 c.c. of Fehling's solution are:—

Arabinose	0.004523 gm.†
Xylose	0.004617 "
Dextrose	0.004753 "
Levulose	0.005144 "
Invert sugar	0.004941 "
Galactose	0.005110 "
Milk sugar	0.006757 "
Maltose	0.007780 "

From this it appears that the two pentaglucooses are the most strongly reducing sugars yet studied, and this is particularly true of arabinose. Both differ from the value for invert sugar sufficiently seriously to effect the accuracy of analyses in which they are concerned but not recognised.‡

C.—Fermentability of the Pentaglucooses.

In connection with the history of arabinose, mention is made by various investigators of its behaviour toward fermenting agents, in which it is regarded as not subject to alcoholic fermentation. In some earlier studies of this body by Prof. Tollens and myself this view was substantiated, and it was further shown that this was a specific property of arabinose, in contradistinction from the true glucoses, galactose, levulose, and dextrose, which are all fermentable, some conflicting views regarding galactose being at that time cleared up.§

* This unusually fine preparation was kindly furnished me by Dr E. W. Allen, of Washington, D.C. who prepared it himself, and to whom my thanks are due.

† Tollens, *Handbuch der Kohlenhydrate*, p. 284.

‡ H. Ost (*Ber. d. Chem. Ges.*, 23, 3006), notes the reducing effect of arabinose on a solution of potassium-copper carbonate, and finds its value lower than that of dextrose, but higher than that of galactose, toward this reagent.

§ *nn. Chem. (Liebig)*, 249, 257; and *Ber. d. Chem. Ges.*, 21, 1374.

In his original paper, in which the discovery of xylose was announced, Koch described the same as non-fermentable, which was somewhat remarkable if it were a true glucose, as was at that time supposed. Its identity as a pentaglucoose being afterwards established, it was of importance to show that it is, like arabinose, strictly non-fermentable, thus fixing this as a character of the $C_5H_{10}O_5$ group. In order to determine the non-fermentability of a given substance it is very essential that such a fermentation test shall be made under conditions favourable to the requirements and activity of the yeast plant used. No better example of this is known than that of galactose, which has been reported non-fermentable by some experimenters, who seemed to have worked with poorly nourished yeast or that deficient in vitality. Where there has been due regard for these conditions, galactose will produce nearly theoretical results of fermentation, although it is plain that it is less rapidly and easily subject to the influence of yeast than its isomers, levulose and dextrose. The method used for xylose was the same as that formerly applied to arabinose. Its special feature consists in supplying the yeast used with a nutrient extract, made by boiling 100 c.c. of the semi-fluid brewery yeast with 100 c.c. of water, and filtering off the dark brown extract resulting. Such a solution contains the natural constituents of the yeast, and, as a nutrient, seems to give better results than artificially prepared solutions of salts.

In the study of xylose two sets of experiments were performed. In one the carbon dioxide produced was collected, and in the other the alcohol. The former were conducted in eudiometer tubes which were first filled to within 15 c.c. of their capacity with mercury; then were added 5 c.c. of distilled water, 5 c.c. of the above-described nutrient solution, 5 c.c. of a mixture of 5 grms. of Fleischmann's compressed yeast with 50 c.c. of water, and lastly the weighed xylose. The tube was then inverted in a mercury trough, and the gaseous products of fermentation were allowed to collect in the upper end. A second tube filled in exactly the same way, but containing cane sugar instead of xylose, was arranged for comparison, and as an index of the activity of the yeast.

For the first experiment were taken 0.139 gm. xylose and 0.1566 gm. cane sugar. Within a quarter of an hour lively fermentation had begun in the cane-sugar solution; and after ten hours seemed practically complete. In the xylose solution no action was observed. After six days, no further action being noticeable, the necessary readings were taken for calculating the amount of gas collected (including that absorbed by the liquid) from the cane sugar. Less than 0.5 c.c. of gas had collected on the xylose solution, too little to indicate any appreciable fermentative action. The gas produced from the cane sugar was wholly absorbed by potassium hydrate solution, and was therefore carbon dioxide. Reducing the temperature and pressure to 0° and 760 m.m., the volume of the undissolved gas from cane sugar was 31.07 c.c., and of that absorbed in the solution, 13.16 c.c., or a total of 44.23 c.c., equal to 78.7736 m.grms., or 50.49 per cent of the sugar used.

In the second experiment were taken 0.1526 gm. of cane sugar and 0.1572 gm. xylose under the same conditions as before. In this case also the cane sugar underwent active fermentation, but no action was observed in the xylose solution. After seven days, measurements of the gas from the cane sugar, which was found to be carbon dioxide, gave a total of 78.506 m.grms., or 51.5 per cent.

The yield of alcohol was next determined in a third experiment. 1 gm. each of xylose and cane sugar was placed in flasks of about 200 c.c. capacity, with 35 c.c. of water, 5 c.c. of the nutrient fluid, and 10 c.c. of the yeast mixture. The flasks were closed with a water-valve. As in the other cases, the cane sugar showed active fermentation, but no action was detected in the xylose. After five days both solutions were neutralised

with sodium carbonate, and after slight dilution, 50 c.c. distilled off and the alcohol determined in the distillates by taking their specific gravities with a Sprengel's specific-gravity flask.

50 c.c. of distillate from the cane sugar solution had the specific gravity 0.9982, equal to 0.472 gm. alcohol, or 47.2 per cent.

50 c.c. of distillate from the xylose solution had the specific gravity 0.9999, showing no appreciable amount of alcohol present.

Summing up the results of these experiments, we have:—

	Carbon-dioxide. Per cent.	Alcohol. Per cent.
1. { Xylose	—	—
{ Cane sugar	50.49	—
2. { Xylose	—	—
{ Cane sugar	51.50	—
3. { Xylose	—	—
{ Cane sugar	—	47.20
Calculated for $C_{12}H_{22}O_{11}$	51.46	48.54

From this it appears that under those conditions which produced almost theoretical fermentation of cane sugar, xylose did not ferment in the least. It is therefore, like its isomer arabinose, non-fermentable, and this becomes a specific characteristic of the pentaglucooses.

It seems, therefore, that the pentaglucooses are of abundant occurrence in nature in the form of gum-like constituents of vegetable tissues; that these bodies are easily converted into the pentaglucooses themselves, and in such form are liable to be confused with the true glucoses, from which, however, they have quite different analytical, and as far as we know economic, values. In addition to the furfural reaction, non-fermentability seems to be a further distinguishing property of the pentaglucooses.

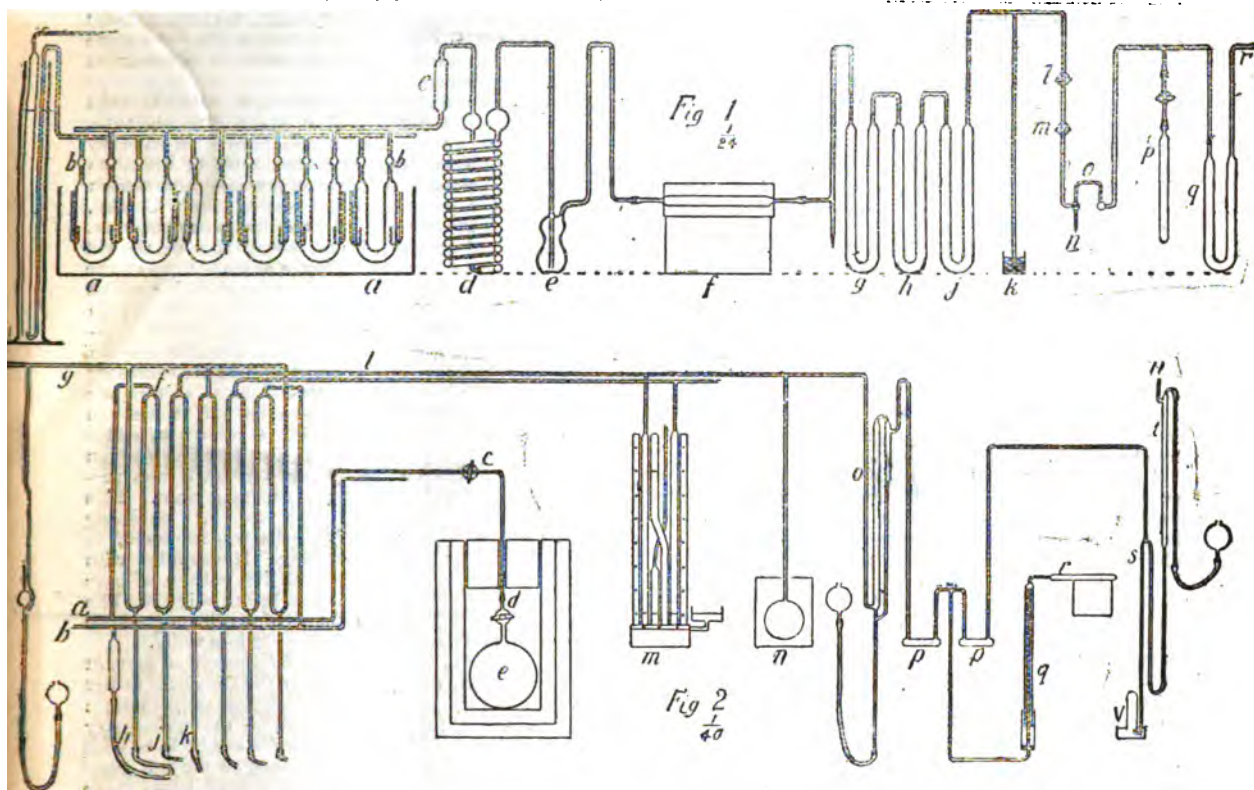
In view of the importance of this group, a method by which they may be determined quantitatively in the presence of the true glucoses seems desirable. Such a method has lately been proposed by Günther and Tollens (*Ber. d. Chem. Ges.*, 23, 1751). Simultaneously with them I have been engaged upon the same subject with somewhat similar results, a more extended report of which is for the present reserved.

THE VOLUMETRIC COMPOSITION OF WATER.

By EDWARD W. MORLEY.

UNTIL recently our knowledge of the volumetric composition of water depended on the results of Humboldt and Gay-Lussac. They presented their memoir to the Academy of Sciences at Paris. The memoir was printed in full in the *Journal de Physique*, vol. ix., p. 129, and translated in Gilbert's *Annalen der Physik*, vol. xx., p. 38, 1805. Chaptal and Berthollet made a report on the memoir to the Academy, which is contained in the *Annales de Chimie et de Physique*.^{*} Humboldt and Gay-Lussac made twelve experiments with an excess of hydrogen, and twelve with an excess of oxygen. They determined the amount of nitrogen in their oxygen by absorption with an alkaline sulphide, and with this oxygen determined the amount of nitrogen in the hydrogen. The mean error of the measurement of the residue after explosion with an excess of hydrogen was one part in five hundred, and in the experiments with excess of oxygen, one part in two hundred and fifty. From the experiments with excess of hydrogen they deduce 1.9989 as the measure of the ratio sought; from the experiments with excess of oxygen, they infer that both series together justify the conclusion that one hundred volumes of oxygen

^{*} Vol. lili., p. 299, 1805.



combine with very nearly two hundred volumes of hydrogen. They do not compute the ratio from the experiments with excess of oxygen: it would be 1'982. Since I began experiments on the matter, Scott has published several statements of his results. In his first paper,* he gives the results of twenty-one experiments. He gives two sets of values of the ratio sought; one computed on the assumption that the impurities found in the residue after explosion were originally distributed proportionally between the two gases, and the other on the assumption that all the impurity was contained in the oxygen. From the whole twenty-one experiments he gets the two values 1'9857 and 1'9941 respectively; excluding two experiments in which the impurity was very great, he gets 1'9897 and 1'9959; from the best four experiments he gets the values 1'9938 and 1'9964; from the six best, he gets the values 1'9938 and 1'9967. The mean error of a determination was one part in two hundred and fifty on the first assumption, and one part in five hundred on the second. Rejecting the two worst experiments, the mean errors become one part in five hundred and one part in seven hundred and fifty parts. He gives the value 1'994 as the most probable value of the ratio sought; but from a consideration of the same experiments, Young† judges that the value of the ratio is between 1'996 and 1'998, and may perhaps be taken as 1'997.

In the autumn of 1887, Scott‡ stated that he had then made over thirty experiments, and gave the most probable value of the ratio as 1'996 to 1'997. In the spring of 1888, Scott§ published four other experiments with a new and larger apparatus; their mean is 1'997; the gases used sometimes contained as little impurity as one part in fifteen thousand. In the autumn of 1888, Scott|| stated

that the volume of hydrogen required seemed to decrease when it was evolved continuously from the same apparatus; and that the variation showed some impurity at present undetected. He published the results of four experiments giving values varying from 2'000 down to 1'995.

My own experiments on this matter are a part of one of my processes for determining the ratio of the atomic weights of oxygen and hydrogen. In this determination the ratio of the densities of the two gases under ordinary conditions is one factor, and the ratio of their combining volumes under the same conditions is a second factor. Since it is difficult to free hydrogen from nitrogen, I hoped to obtain it free from every other impurity, and to determine the amount of nitrogen contained in it, so that I could compute a numerical correction to the observed density. I have now finished the determination of the combining volumes of the gases unless some as yet undetected error should necessitate further investigation. I have been able to reduce the mean error of a determination to less than one half of that which I ventured to predict early in the volumetric studies preliminary to the actual determination.* As the degree of accuracy which I hope it will be found that I have attained is very considerably greater than in determinations of the same kind by others, I have thought it needful to give a somewhat minute account of the details of the work, in order that those interested in the matter may better judge what degree of confidence may fairly be reposed in the result, or may be in a position to suggest improvements or corrections needed in my processes. Though some parts of the work go back for many years, yet, thoroughly agreeing with the expression of Ostwald that he undertakes a heavy responsibility who publishes values of constants, I have made public no figures obtained till I have done the best that I know how to do.

* *Proceedings R. S.*, vol. xlii., p. 398.

† *Nature*, vol. xxxvii., p. 390, 1888.

‡ *Br. Assoc. Trans.*, 1887, p. 668.

§ *Nature*, vol. xxxvii., p. 439, 1888.

|| *Br. Assoc. Trans.*, 1888, p. 631.

* *Am. Chem. Journal*, vol. x, p. 23, 1888.

Preparation of Pure Hydrogen.—The preparation of pure hydrogen has been difficult. I tried long to obtain it by the action of dilute acids on zinc. It is in this way not difficult to obtain a gas free from arsenic and sulphur (or chlorine), and easy to obtain it free from oxygen by passing the hydrogen over heated copper; but two difficulties remain, one of which is serious. The amount of hydrogen which can be obtained from a given weight of materials is not always enough to sweep out all the nitrogen present in the apparatus or contained in the liquids used and still leave much of the gas to be utilised. Perhaps, by constructing the apparatus so that it can be repeatedly exhausted, this difficulty could be overcome. But a difficulty which I have not yet surmounted proceeds from impurities found in every sample of zinc which I have heretofore obtained. The metal contains gases which were absorbed by it during metallurgic processes; of such gases, carbon dioxide is but one; this could be easily removed, but there are present other gases which contain carbon; until they shall have been sufficiently investigated it is not certain whether they can be removed by absorption.

It is to be noted that this last difficulty is by no means removed by amalgamating the zinc, and using it as one pole of a voltaic element or of a decomposing cell. The best zinc I have found gave when so used hydrogen which after combustion in no very long time caused a precipitate in lime water. The gas also contained nitrogen which came from the zinc employed;* I therefore abandoned for the present the use of zinc. Dr. W. H. Burton kindly distilled in a vacuum for me some kilograms of so-called perfectly pure zinc; with which product I shall some time resume the preparation of pure hydrogen.

Having abandoned, perhaps too hastily, the attempt to get pure hydrogen from zinc, I resorted to electrolysis. The decomposition of an alkaline hydroxide seemed promising; by it one would expect to get nothing but hydrogen, oxygen, hydrogen dioxide, and ozone. From the decomposition of absolutely pure potassium or sodium hydroxides, no doubt this pleasing ideal might be realised. But two decomposing cells which I constructed for the purpose and filled with so-called pure potassium hydroxide yielded hydrogen containing carbon. This might possibly come from organic matter adhering to the interior of the cells, although I was at that time especially on my guard against carbon; but it was more probable that it came from the simultaneous electrolysis of an alkaline carbonate. I therefore made a new decomposing cell most carefully of clean glass and platinum, cleaned it from organic matters derived from glass blowing manipulations by long immersion in chromic acid, but filled it with potassium hydroxide to which I purposely added potassium carbonate. The electrolysis of this solution yielded hydrogen which instantly clouded lime water on combustion. It was therefore plain that the alkaline solution submitted to electrolysis must not contain any carbonate. This might no doubt be attained by using barium hydroxide, either alone, or added to potassium hydroxide to remove carbon dioxide. But since the so-called pure potassium hydroxide is purified by solution in alcohol, it is by no means certain that it may not contain carbon other than that existing in an alkaline carbonate. The matter, therefore, began to assume such an aspect that I resorted to the use of sulphuric acid.

Decomposing Cell for 25 Litres an Hour.—I have at command, through the courtesy of the East Cleveland Railroad Company, by day and night an electromotive force of five hundred volts. It was obviously proper to use the current from this source by passing it in succession through many small decomposing cells, rather than through one large cell. It was convenient to have at command a current of hydrogen up to twenty-five litres an hour. To obtain this from a single cell would require a current of some fifty amperes, consuming thirty-three

horse-power. But if a current of one-thirtieth this amount is passed through thirty cells in succession, the same amount of hydrogen is obtained from one horse-power. I therefore sealed thirty decomposing cells to two delivery tubes, so that when the electric current is passed through them, the hydrogen produced is all given off at one tube, and the oxygen at the other. These cells were made by an eminent firm in Germany; twenty-six of them, on treating them precisely as those of my own construction had been treated, cracked at the bottom of the U-tube, having been obviously bent at too low a temperature. After this dismal accident, I had myself to make the set of decomposing cells shown in Fig. 1 at *aa*. Each of the six cells shown is the front one of a column of five which are fused into the transverse delivery tubes shown in section at *bb*. Six such columns are fused to the longitudinal delivery tubes. It is convenient to immerse the cells in water to keep them cool; it is therefore necessary to insulate each electrode in a glass tube as seen in the figure. The oxygen produced was led off to the tall cylinder seen to the left, containing a column of water such as to make the pressure on the escaping oxygen nearly equal to that on the hydrogen when it was permitted to escape at the end of the purifying train. This oxygen was sometimes utilised, as for oxidising copper. The set of decomposing cells was supported in a copper trough for water for cooling. It was filled with distilled water containing one-sixth its volume of pure sulphuric acid, which I distilled just before using it. The decomposing cells had a capacity of six litres; a little more than five litres dilute acid was put into them.

Purifying Train.—At *cc* is an enlargement to prevent the passage of acid over into *d** when the current is rather rapid. *d* contains a 50 per cent solution of potassium hydroxide. *e* contains sulphuric acid for the preliminary drying of the gas. In the furnace at *f* is a tube filled with copper; this tube of hard glass is joined to the soft glass tubes of the rest of the apparatus by ground joints made tight with syrupy phosphoric acid. As this part of the apparatus was not exhausted, no difficulty was experienced in keeping the joints tight. At *g* is a tube containing glass beads and sulphuric acid; this (as well as the two following tubes) lay horizontally, so that the acid should remain well distributed throughout the beads. At *h* is a tube filled with powdered potassium hydroxide, and at *j* is a tube filled with glass wool and phosphorus pentoxide. At *k* is a vent through mercury; at *m* are two glass stop-cocks in succession, which have been lubricated with syrupy phosphoric acid. Their office is at present simply to regulate the flow of gas when the valve at *o* is opened.

At *o* is a valve consisting of glass tubes containing plugs of fusible metal. Two tubes which are perpendicular to the plane of the paper are seen in section; between them are placed several inverted U-tubes. Each one contains a plug of metal; when it is desired to admit hydrogen to the part of the apparatus to the right of the valve, one of the plugs is fused; when it is desired to close the valve, the glass tube is fused together. It may be noted that with a proper composition of the metal, these valves make a joint as tight as could be desired, and that there was no failure by the splitting of the glass tube. By having several of these tubes it was possible to make and again to cut off the connection between the two parts of the apparatus as often as desired. Of course new tubes were put in before each experiment: in this way air was admitted to the tube between the valves *o* and the stop-cock *m*, but air never was admitted into the part of the apparatus to the left of *m* except by fracture of the apparatus. To remove the air from the tube *mo*, a tube was provided as shown at *n*; from which hydrogen was permitted to escape for a long time before each experiment. When *n* was closed by

* The individual parts of the apparatus are drawn accurately to scale, as noted; but the connections between parts are represented more compactly than in the actual apparatus.

fusion, one of the valves at *o* was opened and the connecting tube between *m* and *o* was exhausted by the pump which had exhausted the apparatus to the right of *o*. During this exhaustion the two stop-cocks *m* had to withstand a difference of pressure equal to that of the atmosphere. This they could not do without permitting some leakage of hydrogen into the vacuum which was then producing to the right of *m*. This, however, gave no difficulty, the exhaustion of the large volumes *e* and *n* had already been accomplished under the security of the perfectly tight metal valve, and then these were shut off, so that the leakage during the subsequent exhaustion of *m o p q r*, Fig. 1, and *n c d*, Fig. 2, was so slight that a vacuum of 1-50000 could be obtained in the small volume in question.

It was desirable that the hydrogen to be analysed should not pass over any organic lubricant unless the lubricant were proved not to give up any carbon compound to the gas. Rather than investigate lubricants, I used syrupy phosphoric acid on the glass stop-cocks, and at first used no fusible metal valves, but prevented leakage while the exhaustion of the large volumes *e* and *n*, Fig. 2, was in progress by maintaining a vacuum between the two stop-cocks by means of a second mercurial pump; but the manipulation was troublesome, and if the exhaustion was interrupted, the whole labour had to be recommenced.

In some of my experiments, I used hydrogen purified by the process suggested by Chirikoff,* namely, by utilising the power of palladium to absorb hydrogen, and to give it off again at a higher temperature. In such experiments, a tube containing palladium was connected as shown at *p*, but a tube containing phosphorus pentoxide should have been shown between *o* and *p*, intended to arrest any aqueous vapour which might possibly be given off by the syrupy phosphoric acid at *m*. A second drying tube was placed at *q*, to answer the same purpose for the gas which should pass directly to *r* and the following parts of the apparatus.

The apparatus so far described serves to prepare pure hydrogen. In the case of all impurities to be feared, except oxygen and nitrogen, their absence is capable of proof by direct experiment, as sensitive reagents are applicable. It was not expected that hydrogen free from nitrogen could be prepared, and apparatus designed to measure the residual nitrogen was constructed, and will shortly be described. The only question remaining is as to the possible presence of oxygen after the hydrogen had passed the tube containing heated copper at *f*. To determine how much of a given substance fails to be absorbed by the best absorbent of the substance can be determined commonly only by indirect means which are of limited application. But in regard to the absorption of oxygen by hot copper, I think we can answer the question, and can perhaps also judge whether the presence of a great quantity of hydrogen will lessen the completeness of the absorption. If we pass a current of air containing a little aqueous vapour through a tube filled with phosphorus pentoxide, and also pass a current of air over heated copper in another tube, we can in some sort compare the activity of the two absorptions by observing how far each absorbent is visibly affected. I think we may judge that the copper is not enormously less active than the phosphorus pentoxide. Suppose the phosphorus pentoxide is a hundred or a thousand times more active. Now, partly to obtain a solution of the present problem, I have determined† the amount of aqueous vapour which fails to be absorbed by a phosphorus pentoxide tube containing 25 c.c., when the rate of the current of gas is two litres an hour; the volume of the aqueous vapour left unabsorbed is not more than a thirty-millionth of that of the air. If then we make the surfaces exposed and the time of exposure comparable for the two absorbents, we may expect that the copper will permit not over a hundred or a thousand times this quantity to escape; by increasing the

exposed surface, and the time of exposure, the absorption may be made as complete as we please, for at the temperature used, we have reason to believe that the reaction between copper and oxygen is not reversible. Considering also the action of hydrogen which accompanies the oxygen and is heated with it, it seems to me impossible to suppose that the gas of my experiments contained any such quantity of oxygen as 1-200000 its volume.

Purity of the Hydrogen Obtained.—Each time when a globe was filled with hydrogen for the determination of density, the amount of nitrogen in the hydrogen was determined. The first trial was made when a current of two or three litres an hour had been evolved for three days; the gas then contained 0.00035 volumes of nitrogen. The amount became gradually less as the amount of hydrogen obtained from the apparatus increased. When the apparatus was not in use, it was always left closed by fusion against the entrance of nitrogen except by diffusion through the water in which the oxygen delivery tube ended. When about six hundred litres had been obtained, it became difficult to detect nitrogen; that is, its amount was less than one part in one hundred thousand. Sometimes concordant determinations of the amount of nitrogen showed only one part in two hundred thousand.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

April 16th, 1891.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

MESSRS. J. C. Ayland, J. E. Marsh, G. A. Pingstone, and G. H. Robertson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Duncan, 10, Plough and Harrow Road, Edgbaston, Birmingham; Alfred John Gregory, The Bays, Knights Hill, West Norwood, S.E.; John Knowles, Northwich, Cheshire; Frank H. Leeds, 29, Bouverie Road, Stoke Newington, N.; Robert Andrew Scott Macfie, Rowton Hall, Chester; Frank O. Solomon, North-Eastern County School; Dr. Otto Carl Weber, Reckory Road, Crumpsall, Manchester; Seward W. Williams, East Orange, New Jersey, U.S.A.

The following papers were read:—

5. "Studies on the Formation of Substitution Derivatives." By H. GORDON, M.A.

The following notes relate to a part of a series of investigations undertaken by the author, in the laboratory of the Central Institution, with the object of throwing further light on the laws which govern substitution in the case of benzenoid compounds. It was stated by Armstrong in 1875 (*Chem. Soc. Journ.* 520), that when *parabromodiorthonitrophenol* was warmed with bromine, it underwent isomeric change into *orthobromomorthoparadinitrophenol*. Several other cases, in which, perhaps a similar change takes place, were briefly discussed in the same paper. The author, at Dr. Armstrong's suggestion, has revised these observations, and, while confirming the main result, is able to correct and explain others.

The Action of Bromine on Diorthonitrophenol.—The action of bromine on an acetic acid solution of diorthonitrophenol was found to give, at ordinary temperatures, the normal product, namely, *parabromodiorthonitrophenol*. On the other hand, when the mixture was heated for a short time at 100°, the product consisted of a mixture of the two isomers, *parabromodiorthonitrophenol* and *orthobromomorthoparadinitrophenol*. This mixed product by continued heating at 100° with small quantities of bromine was gradually converted into *orthobromomorthopara-*

* *Journal Russ. Phys. Chem. Soc.*, 1882, Chemical Part, p. 47.

† *American Journal of Science*, vol. xxiv., p. 199, 1887.

dinitrophenol. *Parabromdiorthonitrophenol* is therefore completely converted by the action of heat and bromine into the isomeric *orthobromodinitrophenol*.

In connection with the above facts, it is of interest to note that, whereas Körner (*Gaz. Chim. Ital.*, 1874, 327—397), found that on nitrating crude bromphenol, *parabromdinitrophenol* was obtained, Hübner and Brenken (*Ber.*, 6, 170), obtained *orthobromdinitrophenol*. At the time, Armstrong suggested that these facts might be explained by assuming that Hübner and Brenken had carried out the nitration in such a way as to condition isomeric change. Some experiments were made with the view to ascertain whether nitric acid would bring about this change, and it was found that by heating an acetic acid solution of *parabromdiorthonitrophenol* with a few drops of nitric acid at 100° for a short time, the whole was converted into the isomeric *orthobromdiorthonitrophenol*.

At this point it was thought important to ascertain whether similar changes could be brought about in the corresponding chloro-compounds. Some difficulty was encountered in preparing the *parachlorodinitrophenol* from *diorthonitrophenol*, and it was found that chlorine had no action on the phenol dissolved in acetic acid at 100°, even in the presence of iodine. The chlorination was effected by passing chlorine into a solution of *diorthonitrophenol* in antimony pentachloride heated to about 105°. Only the normal product, *parachlorodinitrophenol*, was obtained.

Action of Bromine on Parachlorodiorthonitrophenol.—Various experiments were carried out under different conditions to ascertain whether any isomeric change could be effected by the action of bromine on *parachlorodinitrophenol*, but in every case with negative results, the normal product, *parachlororthobromonitrophenol*, being formed in every case and no isomer. The result appeared to be in opposition to results published by Ling (*Chem. Soc. Journ.*, 1887, 789), which stated that the action of bromine at 100° on *parachlororthonitrophenol* is to form *parabromorthochlororthonitrophenol*. Ling, however, on repeating his experiments (*Chem. Soc. Journ.*, 1889, 588), found that his former statement was incorrect, and that no isomeric change had taken place. The author considers that the probable explanation of the isomeric change observed in the case of *bromdinitrophenol* is that the bromine first combines with the nitro-compound, and that, at the moment of breaking up, the bromine and NO₂ change places; in the case of the chlorine compound, a similar change does not take place, probably because the chlorine is more firmly held than bromine.

Action of Sulphuric Acid on Orthoparadichlorphenol-orthosulphonic Acid.—In the paper to which reference has already been made, Armstrong indicates that possibly, by the combined action of heat and sulphuric acid, *orthoparadichlorphenolsulphonic acid* could be converted into the isomeric *diorthochlorparaphenolsulphonic acid*. As this would be a very remarkable change, the experiments were repeated under a great variety of conditions of temperature, &c., but in no case was such a change found to take place. Armstrong was no doubt misled by the presence of some *diorthochlorphenol* in his *orthoparadichlorphenol*, prepared by the action of chlorine on phenol, which gives rise to both *dichlorphenols*. It appeared possible that, although no isomeric change took place in the case of *dichlorphenol*, yet it might occur in the case of the corresponding *dibromphenol*. The results tended to show that this was not the case; but as several secondary reactions set in, such as the formation of *tribromphenol*, &c., this reaction was not further investigated.

The Chlorination and Bromination of Phenol.—Phenol, when chlorinated in the ordinary manner, yields a mixture of para- and ortho-chlorophenol (Peterson and Bähr-Predani). As shown by Dubois in 1867, phenol may also be chlorinated by means of SO₂Cl₂, but it was not known whether the product in this case was a mixture of the two isomers; the author has therefore examined it, and finds

it to be a mixture similar to that obtained by means of chlorine alone.

Further, he has investigated the action of bromine on phenol under the conditions described by Hübner and Brenken (*Ber.*, 6, 170), and finds that the product is practically pure *parabromonitrophenol*. If it be assumed that the initial action of chlorine and bromine on phenol is to form an additive compound, which then becomes resolved into hydrogen chloride or bromide and the mono-substituted phenol, it would appear that, at the moment of change, the resulting ortho-compound, in the case of bromine, at once undergoes conversion into the para-derivative; but in the case of chlorine this only partially takes place, owing to the chlorine being more firmly held.

The Sulphonation of the Nitrophenols.—*Orthonitrophenol* and *paranitrophenol*, according to experiments published by Armstrong (*Chem. Soc. Journ.*, 1871, 175), are both readily acted upon by SO₃HCl; the former yields the well-known sulpho-acid; the product from the latter, however, is decomposed by water and is not identical with the sulpho-acid subsequently obtained by Post. It was to be supposed that the product obtained by Armstrong was the sulphate, and this the author finds to be the case. It is scarcely probable that the initial action is different in the two cases; it is more likely that the sulphate formed from the *orthonitrophenol* at once undergoes isomeric change, and that, owing to its greater stability, does not occur in the case of the *paranitrophenol*. The author did not succeed in obtaining any sulpho-acid by heating at 100° the sulphate from the *paranitrophenol*. On adding SO₃HCl (2 mols.) to *paranitrophenol* (1 mol.) and heating at 100°, however, a not inconsiderable amount of sulpho-acid was formed, although much of the material was carbonised.

There can be little doubt, therefore, that the *paranitrophenol-sulphonic acid* is formed by the sulphonation of the previously formed sulphate.

Metanitrophenol closely resembles the para-compound in being readily converted into the sulphate, but not into the sulpho-acid even by the action of heat. The author is engaged in further investigating the action of sulphonating agents on *metanitrophenol*.

DISCUSSION

Mr. A. R. LING said that unfortunately he had made a mis-statement in his work on isomeric change (*Trans.*, 1887, 789), and he wished to thank Mr. Gordon for pointing it out; he had, however, corrected it in a subsequent communication (*Trans.*, 1889, 588). In the latter paper he had recorded a case of isomeric change (when *orthochloroparabromophenol* is nitrated), similar to that observed by Hübner and Brenken, cited by the author. Referring to the action of SO₂Cl₂ on phenol and its derivatives, Mr. Ling said that he agreed with the author that this agent yielded the same mixture of monochloro-derivatives as chlorine alone; he remembered, moreover, having once made an experiment to prepare *dichlorophenol* from SO₂Cl₂ and phenol, and finding that the reaction apparently stopped at the formation of the monoderivative; this was the more remarkable as *parabromophenol* may readily be chlorinated by SO₂Cl₂ (*cf. Trans.*, 1889, 587). His experience of the difficulty of obtaining chloro-derivatives of the nitrophenols by acting on the latter with chlorine was the same as Mr. Gordon's, and on this account he preferred to prepare the chloronitrophenols by nitrating the chloro-derivatives. On other points, including the tendency of the bromonitro-derivatives to undergo isomeric change, and the apparent absence of this property in the case of the chloronitro derivatives, their results were in complete accord.

6. "Compounds of Dextrose with the Oxides of Nickel, Chromium, and Iron." By ALFRED C. CHAPMAN.

The author describes compounds of dextrose with the oxides of nickel, chromium, and iron respectively. The nickel compound was prepared by adding a solution of

nickel hydrate in strong aqueous ammonia to a concentrated solution of dextrose in 90 per cent alcohol. It is a green, amorphous substance, insoluble in water and alcohol, of the formula $C_6H_{12}O_6 \cdot 2NiO + 3H_2O$.

To prepare the chromium compound, an excess of dextrose is dissolved in an aqueous solution of chromic chloride, and this solution is poured into an excess of cold strong ammonia. The precipitated hydrate partly re-dissolves on standing, and the purple solution so obtained gives, on pouring it into 90 per cent alcohol, a lilac-coloured precipitate of the chromium dextrosate. The dry compound is a slate-coloured, amorphous substance, insoluble in water and alcohol. Its composition appears to be represented by the formula



The compound of dextrose with ferric oxide is prepared by adding a slight excess of ammonia to a solution of ferric chloride in which an excess of dextrose has been dissolved. The red precipitate which at first forms soon re-dissolves on standing, giving a deep red solution. If this liquid be poured into 90 per cent alcohol, a red, flocculent precipitate of the dextrosate of iron at once forms. The moist compound dissolves easily in water, giving a red solution which is decomposed on boiling, but is not decomposed by ammonia, potassic ferrocyanide, or potassic thiocyanate. The dry compound is an orange-red, amorphous substance, insoluble in water and alcohol. It has the formula $2C_6H_{12}O_6 \cdot 3Fe_2O_3 + 3H_2O$.

DISCUSSION.

Remarks were made by several speakers with reference to the possible influence on the composition of such substances as described by the author of variations in the proportions of the interacting compounds, their stability in aqueous solution, and their behaviour towards polarised light. Dr. TIZZARD, referring to the circumstance that the ordinary iron reactions were not manifest in the case of the compound of iron oxide with glucose until after the addition of chlorhydric acid, pointed out that the thiocyanate colouration ordinarily regarded as characteristic of ferric salts was also only developed in presence of certain acids, especially chlorhydric acid. The PRESIDENT, referring to the tendency of chromium to form basic salts, pointed out that the formula of the chromium compound would be analogous to those of the zinc and nickel compounds if it were written $C_6H_{12}O_6 \cdot 2(CrO \cdot HO) \cdot 3H_2O$; the iron compound, however, did not appear to have an analogous composition.

The author, in reply, after describing the behaviour of the compounds when boiled with water, said that he had not yet completed their examination.

7. "A Rapid Method of Estimating Nitrates in Potable Waters." By G. HARROW, Ph.D.

The method depends on the reduction of nitric to nitrous acid by means of zinc dust and chlorhydric acid, in a very dilute solution, in presence of α -naphthylamine and sulphuric acid, the estimation being made by comparing the depth of the pink azo-colouration developed in the solution with that arising on similar treatment of standard nitrate solutions. A beaker, containing 50 c.c. of the water, is placed on a sheet of white paper side by side with other beakers holding 50 c.c. of standard solutions containing 1.0, 0.1, and 0.01 of nitrogen as nitrate per 100,000, and to each is added 10 c.c. of a test solution, prepared by dissolving 1 gram. of α -naphthylamine, 1 gram. of sulphuric acid, and 25 c.c. of chlorhydric acid in about 200 c.c. water, boiling with a small quantity of animal charcoal, filtering, and making up to 300 c.c. A very small quantity of zinc-dust—7 to 8 milligrams.—is added to each beaker. If nitrate be present in the water, a more or less intense pink colour is developed, which may be compared, at the end of 15 minutes, with that arising in the standard solutions. By diluting the water until the tint produced is judged to be of the same intensity as that of one of the standards—preferably the most dilute—a first approximation is

arrived at; and the water, having been diluted to the extent indicated by the results, a fresh experiment is made with this diluted water. When nitrites are present, the amount is estimated in a similar manner prior to the addition of zinc-dust, and due allowance is subsequently made. The author quotes a considerable number of comparisons with the Crum method, which show that very satisfactory results are obtainable.

DISCUSSION.

Mr. WARINGTON said that he looked doubtfully on the method proposed, as nitrous acid was not the only product of the action of zinc. The result would be accurate only if the conditions were precisely the same in the solutions compared. The author was right in making a final experiment in which the solutions to be compared were of the same strength. Quantitative analysis by means of colour-depths is perfectly safe only when, as in the old Nesslerising method, the final comparison is between solutions of equal strength. In not a few cases the depth of tint produced is not uniformly proportional to the quantity of substances present, very dilute solutions generally giving a weaker tint in proportion to their strength than strong solutions; this is, for instance, the case in the well-known interaction of metaphenylenediamine and nitrous acid. The speaker also questioned whether the method was more rapid than the indigo method.

Professor P. F. FRANKLAND suggested that probably in presence of the naphthylamine, which would tend to destroy the nitrous acid as it was formed, the reduction of the nitrate would be confined to the production of nitrous acid.

8. "The 'Gravivolumeter': an Instrument by means of which the Observed Volume of a Single Gas gives directly the Weight of the Gas—a Preliminary Note." By FRANCIS R. JAPP, F.R.S.

An apparatus for effecting this object has been described by Lunge (*Ber.*, 23, 448; see also *Ber.*, 24, 735); but his method labours under the disadvantage of requiring for each gas a separate apparatus with a special graduation. Thus Lunge's apparatus for measuring nitrogen is a "gas volumeter," with divisions of 0.798 c.c. (further subdivided into tenths), each of which divisions will contain a milligram. of nitrogen under standard conditions. The reduction to standard state is effected mechanically by means of the "regulator" attached to his gas-volumeter.

The author desires to point out how a gas apparatus may be constructed, by means of which, with an ordinary graduation in cubic centimetres, any required single gas may, without observation of temperature or pressure, and without calculation, be measured under such conditions that each cubic centimetre represents a milligram. of the gas. The form of the apparatus is, with slight modifications, that of Lunge's gas volumeter (*Ber.*, 23, 440); the method of employing the regulator is, however, different.

The apparatus consists of two gas burettes of, say 50 c.c. capacity each. One of these is the gas measuring tube; the other performs the function of the "regulator" in Lunge's gas volumeter, and may be termed the "regulator tube." Both are connected, as in Lunge's gas volumeter, by means of stout flexible tubing and a T-piece, with the same movable reservoir of mercury. Both are moistened internally with a drop of water, in order that the gases they contain may be saturated with aqueous vapour.

The 25 c.c. division of the regulator tube is taken as the starting point in calculating what the author terms the "gravivolumetric values" of the different gases to be measured. Thus in the case of nitrogen he calculates to what volume 25 c.c. of "standard-dry" nitrogen must be brought in order that 1 c.c. would correspond with 1 m.grm. of the gas: that is to say, 25 c.c. of standard-dry nitrogen $0.001256 \times 25 = 0.0314$ gram.; and, therefore, these 31.4 m.grms. of nitrogen must be brought to the volume of 31.4 c.c. The division 31.4 on the regulator

tube is marked N_2 . Corresponding points are in like manner determined for the various other gases which it is desired to measure, and these points are similarly marked O_2 , CO_2 , &c., as the case may be, on the regulator tube. Finally, the thermometer and barometer are read (a process which is only necessary once for all in setting the regulator); the volume which 25 c.c. of standard-dry air would occupy if measured moist at the observed temperature and pressure is calculated; and this calculated volume of air is admitted into the regulator tube and the tap closed. The instrument is now ready for use.

Suppose it is desired to ascertain the weight of a quantity of nitrogen contained in the measuring tube. The mercury reservoir is lowered until the mercury in the regulator tube stands at the nitrogen mark, 31.4, at the same time adjusting the regulator tube itself, by raising or lowering it bodily, so that the mercury level in the measuring tube and the regulator tube may be the same. Under these circumstances each c.c. of gas in the measuring tube represents a m.grm. of nitrogen. For since in the regulator tube 25 c.c. of standard-dry air have been made to occupy the volume of 31.4 c.c., and as the gases in the two tubes are under the same conditions as regards temperature, pressure, and saturation with aqueous vapour, therefore, in the measuring tube, every 25 c.c. of standard-dry nitrogen has also been made to occupy the volume of 31.4 c.c. But 25 c.c. of standard-dry nitrogen weigh, as we have seen, 31.4 m.grms.; so that the problem is solved, and the c.c. and tenths of c.c. give directly the weight of the gas in m.grms. and tenths of m.grms.

The various other single (i.e., unmixed) gases may be weighed in like manner by bringing the mercury in the regulator tube to the "gravivolumetric mark" of the gas in question, and adjusting the levels as before. An exception would be made in the case of hydrogen, which would be brought to such a volume that the c.c. would contain a tenth of a m.grm.

Lastly, if the mercury in the regulator tube be brought to the mark 25, a gas or mixture of gases in the measuring tube will have the volume which it would occupy in the standard-dry state. In this form the instrument is merely a gas-volumeter, as described by Lunge, and may be employed for ordinary gas analyses.

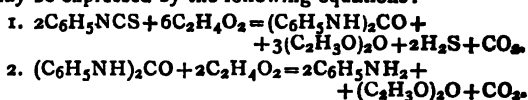
The "gravivolumeter" is thus designed to fulfil a variety of purposes for which Lunge employs a number of different gas-volumeters. Whether it will fulfil these purposes equally well remains to be seen. The theoretical principle is unimpeachable; but there are doubtless practical difficulties to be overcome before the "gravivolumeter" can rank as a working laboratory appliance. Very likely the foregoing (merely provisional) dimensions of the regulator would have to be increased in order to give sufficient accuracy of adjustment. The author proposes to have the instrument constructed in various forms, so as to ascertain the most suitable. He anticipates that it will, at all events, give results sufficiently accurate for technical purposes. Meanwhile he desires, by this preliminary note, to place on record this principle of gas analysis, which he believes to be new—the principle of measuring the various single gases at such a volume that each c.c. contains a m.grm. of the gas.

Mr. DE MOSETHAL exhibited one of Lipmann's "coloured" photographic negatives.

9. "The Action of Acetic Acid on Phenylthiocarbimide." By J. C. CAIN and J. B. COHEN, Ph.D., Owens College, Manchester.

The authors have repeated the experiments of Hofmann, and show that the product of the action of pure glacial acetic acid on phenylthiocarbimide is not diacetanilide as stated by Hofmann; but that two compounds are formed, viz., diphenylurea and acetanilide. The proportion of these products depends upon the temperature at which the mixture is heated. At a lower temperature, diphenylurea is mainly formed, and at a higher temperature, acetanilide.

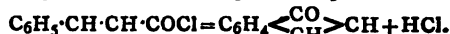
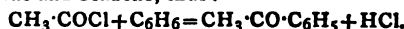
The action, which appears to take place in two stages, may be expressed by the following equations:—



These interactions are independent of the presence of water.

10. "The Action of Aluminium Chloride on Benzenoid Acid Chlorides." By R. E. HUGHES, Jesus College, Oxford.

At Mr. Marsh's suggestion, the author has examined the action of aluminium chloride on cinnamic and hydrocinnamic chlorides in the expectation that pentamethylene derivatives might result from the occurrence of an internal condensation analogous to the external condensation which attends the formation of acetophenone from acetyl chloride and benzene, thus:—



The experiments have, however, afforded negative results. The chloride was either dissolved in or mixed with (in the case of hydrocinnamic chloride) light petroleum, and aluminium chloride was then added; action set in at 80–90° in the case of cinnamic, and at about 50° and more briskly in the case of hydrocinnamic chloride. The chief product in either case was an ill-characterised substance, the nature of which remains to be determined. Both chlorides afforded a small amount of the aluminium salt of the corresponding acid in the form of a microcrystalline powder, insoluble in alcohol, benzene, ether, and petroleum, slightly soluble in a warm solution of sodium carbonate.

The author incidentally describes the following hydrocinnamic derivatives.

Hydrocinnamic chloride, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot COCl$, boils at 117–119°, under 13 m.m. pressure; the author specially points out that the properties of this chloride are strikingly similar to those of benzoic chloride and characteristically different from those of cinnamic chloride, which, unlike most acid chlorides, is a remarkably inert substance, being only very slowly decomposed by water or caustic alkalis.

Hydrocinnamide crystallises from hot alcohol, in which it is readily soluble, in stellate groups of needles melting at 82°; it is readily soluble in hot water.

Hydrocinnamanilide crystallises from hot alcohol in faintly yellow plates melting at 92°.

It is noted that benzoic and cinnamic acids may be readily separated by treating the mixture with phosphorus pentachloride and distilling the product under reduced pressure, the portion passing over below 95° under 10 m.m. pressure contains the benzoyl chloride.

OBITUARY.

THE LATE JAMES BUCKTON MACKINTOSH, C.M.

It is our painful duty to put on record the death of an eminent American chemist, James Buckton Mackintosh, C.M. The deceased, one of the many victims of the prevailing epidemic of influenza or dengue-fever, died at New York on April 15th last. Mr. Mackintosh had made a speciality of the rare earths and was collecting materials for a monograph on the methods for their separation. He was born either at Montrose or Birkenhead, and obtained his chemical education in the Liverpool Schools. In 1873 he emigrated to the United States, and, until his death, resided at Hoboken. We regret that our informant, though an old friend and family connection of the

deceased, has not been able to give us the titles and dates of his researches, having been at the time away from home. For some years he was chief chemist to the New York Consolidated Gas Company and principal assistant to Prof. Eggleston, of the School of Mines.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxii., No. 15, April 13, 1891.

Transformation of Cupreine into Quinine.—E. Grimaux and A. Arnaud.—On comparing the formula of cupreine, $C_{19}H_{22}N_2O_2$, with that of quinine, $C_{20}H_{24}N_2O_2$, these two bodies seem to have the same relation as phenol, C_6H_6O , and its methyl-ether, C_7H_8O . Cupreine being a body of mixed functions, partly a base and partly a phenol, quinine would be its methyl-ether—a view which is completely confirmed by experiments. The natural products extracted from plants often contain the methyl group, but never the ethyl group. The reason for this fact is probably that plants, in absorbing carbonic acid, convert it by a reductive process into methylic aldehyd, and then into methylic alcohol.

The Action of Hydrobromic Acid upon Silicon Chloride.—A. Beeson.—Theory enables us to foresee the existence of three silicon chlorobromides, all of which the author has obtained by the action of HBr upon Si_2Cl_4 .

Thermo-Chemical Study of Platinum Chloride and its Combinations.—L. Pigeon.—This paper does not admit of useful abstraction.

Electrolytic Determination of Rhodium.—A. Joly and E. Leidié.—Rhodium may be electrolytically determined with great accuracy in compounds which contain no other metals save those of the alkaline class. It should be present preferably as chloride or sulphate. An excess of acid delays but does not prevent the deposition of the metal, and the decomposition yields no products save the metal at the negative pole and the products of decomposition of the acid at the positive pole. The present study is the first portion of an extended research which the authors have undertaken on the separation of the metals of the platinum group from each other and from the common metals, such as copper, lead, iron, bismuth, and zinc, which accompany them in their ores.

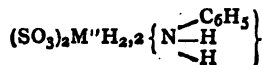
On an Amidoxazol.—M. Hanriot.—This memoir is not adapted for useful condensation.

The Use of Phenylhydrazine in the Determination of Sugars.—M. Maquenne.—The action of phenylhydrazine upon the reductive sugars is the only means of precipitating these bodies in a definite form from solutions in which they are mixed with other substances. The weight of the osazones thus obtained on heating a given weight of the different sugars for the same time with the same quantity of the hydrazinic reagent varies from one sugar to another within very wide limits if we operate under strictly identical conditions.

On a Violet Colouring Matter derived from Morphine.—P. Cazeneuve.—The action of paranitrosodimethylaniline ether upon the phenols or the aromatic amines leads to the formation of indophenols and safranines. With morphia the same reaction leads to the formation of an azine or more probably an indamine. It is a fine violet colour of a definite composition. The author boils for 100 hours in an apparatus furnished with an ascending condenser 7 grms. morphine, 5 grms. para-

nitrosodimethylaniline, in 500 grms. methylic or ethylic alcohol. The compound obtained is amorphous, sparingly soluble in water, very soluble in the methylic, ethylic, and amylic alcohols, in which it shows a well-marked dichroism. It is red by reflected, but violet by transmitted light. It dyes wool, silk, and gun-cotton, directly in a bright violet tone which is not permanent in light. This violet is conjectured to be the first colour derived from a natural alkaloid.

New Compounds obtained with Certain Sulphites of Metals and Aniline.—G. Denigès.—The author studies the compounds by aniline and the cuprous, cadmium, zinc, manganese, ferrous, cobalt, nickel, and mercuric sulphites. These compounds may be represented by the general formula—



They are most easily obtained by treating with an aqueous solution of aniline water, a mixture of sodium bisulphite, and a soluble salt of the metal which it is intended to combine with the aromatic base.

On Aspergilline—a Vegetable Hematine.—Georges Linossier.—The author shows that Dr. Phipson's palmelline has no analogy either with aspergilline or with hematine.

Influence of Neutral Mineral Potassium Salts upon the Solubility of Potassium Bitartrate.—Ch. Blarez.—For potassium chloride, bromide, iodide, chlorate, and nitrate, one and the same influence upon the solubility of potassium bitartrate, other things being equal, is produced by quantities of salts proportionate to their molecular weights.

On the Characteristic of Fig-Wine.—Wine is abundantly made in Algeria from figs. These wines are used to mix with grape wines, and their presence may be detected by the mannite which they contain in the proportion of 6–8 grms. per litre.

A Method for Recognising Margarine mixed with Butter.—R. Lézé.—The author pours 1.5 c.c. of strong syrup into a glass tube, stoppered, and having a mark at 10 c.c. This tube is set in a water-bath at a gentle heat; the butter in question is added in small portions until it reaches the mark 10. The tube is then stoppered and gently agitated, tied to a string and turned round like a sling. In pure butter the fatty matter remains transparent and limpid; the whitish emulsion is bulky and collects well together. In butters containing margarine the fatty matter remains soluble and milky.

Purification of a Phlegm of Molasses Alcohol during Rectification.—D. Mohler.—The rectification of the phlegms gives alcohols of a good taste almost entirely pure, the toxicity of which may be considered nul.

Revue Generale des Sciences pure et Appliquées.
Vol ii., No. 7.

On Electric Discharges in Rarefied Gases and the Constitution of Matter.—W. Crookes, F.R.S.—Concluded from the previous number.

Obituary Notice.—Auguste Cahours.—This illustrious savant, born in 1813, will be honourably remembered as one of the creators of modern organic chemistry. A mere catalogue of his researches would exceed the space at our disposal. He was a member of numerous scientific bodies, including the Academies of Berlin and of St. Petersburg, and in 1868 he reached the great object of his ambition—the membership of the Academy of Sciences of Paris. His private life, from 1867 to 1874, was a tissue of misfortunes, as he lost in succession his brother, his wife, and his two sons.

Justus Liebig's Annalen der Chemie.
Vol. cclv., Parts 1 and 2.

On Crystalline Mercuric Oxichloride and the Determination of Mercury.—J. Volhard.—The oxichloride, $\text{Hg}_2\text{O}_2\text{Cl}_2$, is easily obtained by allowing a cold saturated solution of mercuric chloride, mixed with sodium acetate, to stand for some days, when the crystals form on the surface in groups and sink to the bottom. Mercury sulphide dissolves in caustic alkalis in presence of alkaline sulphides. The solution, which must contain the mercury in the mercuric state, is nearly neutralised with pure sodium carbonate, and is then completely precipitated with ammonium sulphide. It is preferable to use sulphide which has been quite recently prepared from the strongest liquid ammonia. Soda-lye is then added whilst shaking, until the dark liquid begins to clear. It is heated to a boil, and more soda-lye is added until the liquid becomes quite clear. The lye must of course be free from silica, alumina, and all metals precipitable by ammonium sulphide. Soda from metallic sodium is best, ascertaining first that it contains no silver. From the alkaline solution the sulphide is re-precipitated at a boil with a solution of ammonium nitrate. The ebullition is kept up until the ammonia is nearly expelled. If it has to be collected on a weighed filter, the precipitate has to be first washed with boiling water by decantation, and not placed on the filter until the washings no longer react with a solution of silver nitrate.

Revue Générale des Sciences Pures et Appliquées.
Vol. ii., No. 6.

Electric Discharges in Rarefied Gases and the Constitution of Matter.—W. Crookes, F.R.S.—The first part of the Presidential Address delivered before the Institution of Electrical Engineers.

MEETINGS FOR THE WEEK.

- SATURDAY, 9th.—Physical. (At Cambridge).
TUESDAY, 12th.—Institute of Civil Engineers, 8.
— Royal Medical and Surgical, .30.
— Photographic, 8.
— Royal Institution, 3. "Bacteria: their Nature and Functions," by Edward E. Klein.
— Society of Arts, 8. "Glass Painting," by Arthur Kennedy.
WEDNESDAY, 13th.—Society of Arts, 8. "Fast and Fugitive Dyes," by Prof J. J. Hummel.
THURSDAY, 14th.—Royal, 4.30.
— Mathematical, 8.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "Recent Spectroscopic Investigations," by Prof. Dewar, M.A., F.R.S.
— Society of Arts, 4.30. "Description of the Growing Uses of Tussur Silk in the European Textile Manufactures," by Thomas Wardle.
FRIDAY, 15th.—Quekett, 8.
— Royal Institution, 9. "Crystallisation," by Prof. G. D. Liveing, M.A., F.R.S.
SATURDAY, 16th.—Royal Institution, 3. "The Artificial Production of Cold," by H. Graham Harris, M.Inst.C.E.

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THE CHEMICAL NEWS.

VOL. LXIII., No. 1642.

THE CAUSE OF IMPERFECTIONS IN THE COLOUR OF SHEET BRASS.*

By THOMAS TURER, Assoc.R.S.M., F.C.S., F.I.C.,
Lecturer on Metallurgy at Mason College.

DURING the last few years, and particularly in connection with the evening Metallurgical Classes held at Mason College, my attention has frequently been directed to a particular kind of copper-coloured or brown stain, or marking, which not uncommonly occurs on the surface of finished sheet brass. Many sheets are quite free from this imperfection, but in others the stains cover a considerable proportion of the surface, being sometimes in the form of distinct spots or rings, but usually in bands or belts such as one might suppose could be produced by the rolling out of a small globule of copper or rich copper alloy, embedded in a matrix of yellow brass. These imperfections, of which examples are shown, are met with in brasses of varying composition, and are common in button metal, cartridge metal, and other forms of good sheet brass, and their presence frequently involves considerable loss and trouble. Thus, in the case of button metal, the blanks have to be sorted to separate those which are discoloured, and which are therefore unsuited either for use as bright brass or for bronzing or tinning. These discoloured blanks are of inferior value, and are usually japped and sold as black buttons. In many other branches of the Birmingham sheet metal trades, these discolourations are equally troublesome.

A number of explanations have been suggested in order to account for the production of these copper-coloured stains, among the chief being the following:—

1. That they were caused by inattention on the part of the workman in allowing the sheets to become overheated during annealing, by which it is alleged that zinc is volatilised from the surface of the sheet, and a coating of copper produced. To this it may be objected that if such an action took place there is no reason why the copper should be produced in spots or bands instead of a uniform film, as might be expected if the whole sheet were overheated. But in addition it is easy to experimentally prove that overheating does not produce this effect; for if a sheet of brass be heated in a muffle until a portion actually melts, it will still be found, on removing the scale from the remaining portion by pickling, that a fairly uniform colour is obtained.

2. The workmen themselves assert that these stains are due to sulphur in the coal. Of course, "sulphur" as used by the workman includes combustible gases and the products of combustion, and does not necessarily mean the element sulphur at all. But, as in the previous case, it is not easy to see why, if the whole of the sheet is exposed to the same gases, these gases should produce a deep colour in one portion of the surface, and no colour at all on the parts immediately adjacent.

In order to test this matter I heated ordinary sheet brass in a gas muffle to a full red heat, and from time to time introduced fragments of sulphur so as to keep the atmosphere charged with sulphur dioxide. The result is shown in sample 1, the surface of which, after having been cleaned in dilute sulphuric acid, is rather rough and dull, but practically free from the stains referred to. To further test this point, samples 2 and 3 were prepared. On sample 2 flowers of sulphur were sprinkled in the form of a letter S, and the metal was then heated as before.

After pickling, the position of the sulphur is only indistinctly seen on the surface by dark coloured stains. On sample 3 a heap of sulphur was placed, but after heating and subsequently pickling the result obtained was a dark coloured stain with light coloured spots. Obviously, therefore, sulphur or sulphurous gases cannot be responsible for the production of the red stains previously mentioned. But it appeared possible that coal dust or coal ashes, or soot, or a reducing atmosphere, might assist in the reduction of zinc oxide, which is non-volatile, and so assist in liberating zinc from parts of the brass and produce the objectionable red colouration. I therefore tested a number of samples by covering a portion of each of them with coal-dust, coal ashes, charcoal powder damped with a solution of gum, chalk, &c. In each case the result was very similar and is illustrated by sample 4, on which coal ashes were dusted in the form of a letter A, and, after pickling, the pattern is observed to remain as a faint and not very definite dark stain. It appears to me, therefore, that the imperfections we are considering cannot be due to variations in any of the furnace conditions above enumerated.

3. Perhaps the most natural suggestion from the general appearance of the imperfect sheets is that which has met with considerable favour in some quarters, namely, that the brass is not uniform in composition, but that owing either to imperfect mixture or to separation during cooling, the constituent metals have more or less separated in places, and that the red colouration is due to the greater concentration of copper in certain parts. It must be remembered, however, on the other hand, that all trustworthy experiments on this subject have shown the very remarkable uniformity of composition which exists in copper zinc alloys. Dr. Tilden allows me to mention that in connection with his experiments on the "Corrosion and Pitting of Copper and Brass by Saline Waters" (*Journ. Soc. Chem. Indust.*, Feb. 1886), he paid special attention to the question of the uniformity in composition of the sheet metal employed, and as the result of a large number of tests he was unable to find any evidence to support the view that separation of richer copper alloys occurred. The researches of Laurie (*Journ. Chem. Soc.*, 1888, p. 88), also give strong support to Dr. Tilden's conclusions. In one sample of doubtful origin I believe I have obtained distinct evidence by etching with nitric acid that such a separation had taken place, though probably the specimen was from the "spilly" end of the strip, as the little grains of red alloy were distributed in a manner such as might be expected under the circumstances. But by etching a large number of other samples of sheet brass with varying proportions of copper, I have never met with another instance of the same thing, and any such separation must be very unusual.

In order to test this third explanation I have selected a number of strips of sheet brass which were very plainly marked with bright copper-red spots and bands, the markings being on both sides of the sheet, and giving the appearance of nodules of a separated alloy passing through the thickness of the sheet. These strips were etched by immersing in diluted nitric acid for about 12 hours, but the resulting strip was in each case quite uniformly crystalline in texture after the outer surface had been removed, and no indication of variation in composition was obtained. Samples 5 and 6 illustrate these experiments, the part which was etched and now shows a perfectly uniform crystalline character being originally very plainly marked with copper-red discolourations. Further proof that only the surface is affected by these discolourations is afforded by the fact that the copper can be scraped off with a knife, when ordinary yellow brass is found underneath, while, on the other hand, so far as I am aware, these red markings are not laid bare when, in the process of working, the surface is removed from a piece of ordinary bright brass. It appears evident, therefore, that the imperfection of surface cannot be due to

* Read before the Birmingham Philosophical Society, May 6, 1891.

can be adjusted by altering the level of the mercury. When the flow is rather rapid, the bubbles burst with such force as to throw some mercury over into the short wide tube at the right, whence it flows back by the tube provided for the purpose. By the use of this valve, it is possible to exhaust everything to the right of *o*, and then to introduce any required volume of gas from the store in *n*. At *p* are two drying tubes intended simply to prevent aqueous vapour produced at *r* from entering *o* or *s*, and interfering with their action. At *s* is a Sprengel pump. The mercury which operates it first falls through the tube *t*, kept exhausted by a Toepler pump fused to *u*. This trap is made long as shown, so that even when the gas in *p*, *q*, *r* is at atmospheric pressure, mercury falling into *t* has still to pass through many centimetres of vacuum. At *v* is the jar in which the gas is transferred to the measuring apparatus. It is plain that, disregarding for the moment the apparatus *r*, we can, on opening the valve *o*, transfer gas from the store in *n* to the jar at *v*. But the apparatus at *r* has sometimes to perform an office which has made it possible to obtain from impure gases results as accurate as from pure gases. It will be recalled that Humboldt and Gay-Lussac obtained, although they worked with very impure gases, results whose mean errors are comparable with those of Scott, whose gases were far purer. This was owing to the fact that they devised means for measuring the impurities of one gas by some process other than the eudiometric explosions which determine the total nitrogen in both gases, and also the volume of the gas which has disappeared in the explosion. If Scott had succeeded in refining on the methods of Humboldt and Gay-Lussac in this respect as much as in his methods of preparing and measuring the gases, he might well have attained a degree of accuracy satisfactory to himself and answering the present demands of science. The apparatus *r* was designed to make possible the determination of the nitrogen contained in the hydrogen used. It consists of a hard glass tube filled with copper oxide, and united to the rest of the apparatus by means of a mercurial seal. The apparatus to the right of *n* was duplicated for oxygen, except that the tube *r* contained copper instead of the oxide, and no drying tubes *pp* were needed.

To get copper oxide which could be heated in a vacuum without giving off gas cost much trouble. Electrotype copper was oxidised in a current of oxygen; but when it was heated in a vacuum, it gave off a gas for a long time. In some cases, heating for several days answered the purpose; but some samples had to be rejected and the heating re-commenced with a new sample. The gas given off was mostly absorbed by potassium hydrate, but as yet has not been further studied.

The mano barometer *m* served partly in preparing for weighing the gas in the globe *e*, and partly in preparing for determining the amount of nitrogen in the hydrogen by means of the apparatus *r*. For the last purpose, an accuracy permitting readings to a thousandth of an atmosphere was sufficient; the apparatus will therefore not be described at present.

Apparatus for Accurate Measurement of Volumes of Gases.—My measuring apparatus has finally become rather elaborate. It is shown in Fig. 3. It is mounted on a stone pier, independent of the floor of the room in which it stands. The eudiometer and measuring tube ends above in a stop-cock and recurved tube whose end is seen to emerge inside the left hand gas jar in the cistern. The stop-cock is manipulated by means of a metal shaft and long handle, seen at the top of the column which carries the reading microscope. At the bottom of the eudiometer is a glass stop-cock of large bore intended to facilitate the washing out of the eudiometer after an analysis. For this purpose the glass plug of the stop-cock is withdrawn and a duplicate plug inserted in which there are such connections that the part below the stop-cock is shut off, and an opening is left between the eudiometer and the outside of the apparatus. By con-

necting the top of the eudiometer to an air pump, aqua regia or potassium hydroxide can be drawn into the eudiometer; then by connecting the bottom of the eudiometer to the pump, distilled water can be drawn in at the top. In this way the tube was kept so clean that carbon dioxide was formed only twice, when this washing was omitted; accurate reading of volumes were also

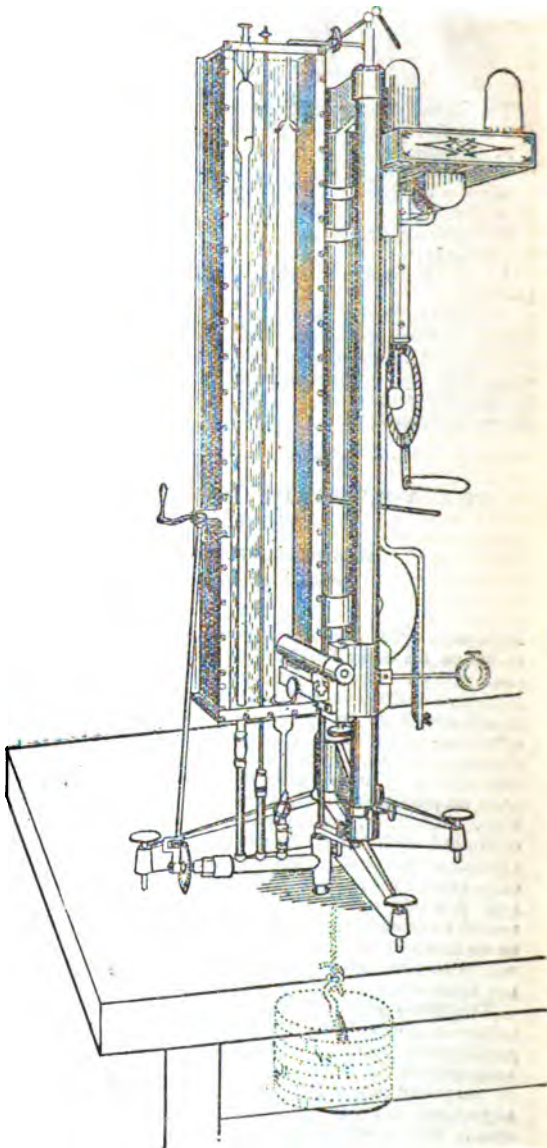


FIG. 3.

facilitated. Below the glass stop-cock, the eudiometer is connected by a rubber connector to a steel tube screwed into an iron stop-cock. The key of this stop-cock is prolonged upwards some four decimetres, and ends in the handle seen just above the reading microscope. A small wheel imperfectly seen under the reading microscope carries a series of stops of which any one can be brought into position so as to arrest the opening of the stop-cock at a determinate point. This stop-cock governs the admission of mercury from the movable reservoir carried vertically by an apparatus placed on a table to the left,

The iron stop-cock has three steel tubes which are connected, one to the eudiometer as said before, the others to the two pressure tubes; the smaller of these is an auxiliary, used for all rough measurement, so as to reserve the other for the final accurate measurement. This tube is shut off from connection with the other tubes by a piston valve whose motion is produced by the geared wheels seen at the left of the iron stop-cock. Its vacuum was easily kept unimpaired for months, as was proved by repeated determinations. But further, this piston valve also served as a micrometric adjustment of the level of the mercury in the eudiometer and pressure tubes. The use made of this will be mentioned below, and it contributed greatly to the accuracy obtained. These three tubes were enclosed in a box with glass front and back, and filled with clear water kept stirred by a current of air. The eudiometer is secured into a brass plate which is ground water-tight to the bottom of the box; on removing a clamp, the eudiometer can be lifted out of place if necessary, and can be replaced without a variation of its level amounting to the hundredth of a millimetre. It was convenient to compute the measured volumes of gases by means of an interpolation formula whose constants depended on the relative levels of fiducial marks on the eudiometer and pressure tubes, and constancy of this relation even after removing the eudiometer was highly desirable. The pressure tube was provided with a fine screw motion by which it could be adjusted vertically while in position and filled ready for use.

The recurved tube at the upper end of the eudiometer serves for the introduction of gas into the apparatus. The cistern containing the jars of gas is capable of the motion required to bring the open end of this recurved tube inside of the jar *a b* and to its top. When the cistern is in its highest position, the recurved tube is wholly contained within the well seen under the cistern, and the cistern can be moved vertically by a distance equal to the height of the tallest jars used. It is fitted with sliding ways, counterpoised, and moved by a screw; by means of a multiplying gear, its motion can be made as rapid as is convenient; by means of the adjustable counterpoise, the cistern with its 35 kilograms of mercury can be moved up and down and placed accurately at the required level with ease and safety. In the centre of the cistern is a well for filling the jars used; the rest of the bottom is inlaid with a smooth surface of slate. Care was taken to have no crevices in which air could be entangled, from which perhaps it should rise into a jar of gas. The mercury was always kept as much as three centimetres deep, to lessen the probability that gas in the jars should be contaminated by diffusion between the walls of the jar and the mercury in contact with them. But the danger of this contamination is very slight. I left two jars of hydrogen standing in the cistern for eleven weeks, after which time I was unable to detect any contamination. The reason of this, so different from the result obtained by Faraday,* is probably the great care taken in filling the jars with mercury. The jar was always put entirely under the surface of the mercury while it was closed with a glass plate, so that no dust from the free surface of the mercury could get to the inside of the jar.

The vacuum in the pressure tube was obtained by exhausting the tube from above while the bottom was closed, then admitting mercury till it rose above the glass stopper at the top of the tube; during the exhaustion, the stopper was loosely in place, and was in the vacuum. When the stopper was covered by mercury, it was forced into place; a drop of water had previously been put in the upper part of the pressure tube. In the pressure tube were two Jolly points, of which sometimes one was used, sometimes the other, an interpolation formula having been computed for each of the two systems of pressures measured by the mercury when brought to one of the

points. The vacuum in the pressure tube was often measured, or rather, the real zero of pressures was determined by producing a good vacuum in the eudiometer, bringing the mercury in the pressure to one of the Jolly points, and observing the level of the mercury in the eudiometer; this level was the zero from which pressures were counted, and could be verified as often as desired, and did not change during the series of experiments.

The measurement of the reduced volume of a gas is effected by adjusting the apparent volume till the mercury in the pressure tube stands at one of the Jolly points, and measuring the level of the mercury in the eudiometer. This reading determines the apparent volume, and the difference between this reading and the reading of the zero point gives the pressure under which the gas is measured. A convenient interpolation formula reduces the computation to the addition of a constant to the reading, taking the doubled logarithm of the sum, and adding a logarithmic constant.

The measurement of the level of the mercury in the eudiometer is made by means of a reading microscope. This is carried on a cylinder supported on the framework of the instrument, and provided with a tangent motion. On this cylinder slides a piece which can be tightly clamped, and which carries ways on which the microscope can be moved vertically by a micrometer screw. When the microscope is made to give distinct vision of a scale engraved on the eudiometer, the terminal lines of an eyepiece micrometer are made to agree with two successive millimetre divisions of the scale. As these are but the three-hundredth of a millimetre wide, the coincidence can be made accurately. When coincidence is secured, the microscope is made to give distinct vision of the meniscus and the illumination arranged. When the mercury is now made to coincide accurately with one of the Jolly points in the pressure tube, the reading of the fraction of a millimetre by which the mercury in the eudiometer stands above a millimetre division of the scale is accomplished in a few seconds. Great care was taken in the calibration of the eudiometer. For this I used to the end of the recurved tube, mentioned before, a further tube opening downwards. Through this air-free water was introduced into the eudiometer. The mercury reservoir being raised, mercury was admitted by opening the iron stop cock against the proper stop. Water then began to drop from the added tube. The rate of admission of mercury must be so slow that the amount of water left adhering to the inside of the eudiometer is small, and is nearly constant from one experiment to the next. Three hours for the admission of eighty centimetres of mercury gave concordant results. When the mercury reached the lowest point to be calibrated, the iron stop cock was closed, and the level of the mercury and the temperature of the water determined. The tube from which the water had been dropping was wiped in a constant manner, and a tube put in place to collect the water which now issued on opening the iron stop-cock. When the mercury rose to the next standard point, level and temperature were measured, and another tube placed to collect water, while the water already issued was weighed. True volumes at zero were computed from the weights and temperatures observed. The calibration was made four times; I give the values found for the points at which oxygen and hydrogen were measured in the experiments, and the differences between the mean and the several determinations. It will be seen that the mean error of a single determination of volume is five cubic millimetres. A tube was previously calibrated with a mean error only three-fifths as much; but it broke during the first experiment. The sky was so cloudy while this the present tube was calibrated, that illumination was defective and work very trying. But in the determination of the volumetric composition of water, any slight errors, either in the calibration of the standard points, or in the interpolation at intermediate points, was nearly eliminated by

* *Annals of Philosophy* (II.), vol. xii., p. 389, 1826; *Poggendorff's Annalen der Physik*, vol. viii., p. 124, 1826.

a proper distribution of the points used in the measurements.

Scale division.	Volume found.	Errors (cubic millimetres).			
		1.	2.	3.	4.
600	184.323	0	12	-7	-4
625	191.849	-3	-4	4	4
650	199.442	1	-2	10	-10
675	207.082	7	-15	2	7
700	214.766	-1	3	5	-7
725	222.460	1	4	-10	5
750	230.132	-1	-3	-1	5

Since, in my way of manipulating, the gas, scale, mercury, and eudiometer are all at the same temperature, the effects of the expansions of all were taken into account in one factor, which, moreover, was determined for the actual degrees of the thermometer used.

In measuring the volume of a quantity of gas in the eudiometer, the mercury in the recurved capillary tube was brought to a certain mark. The level of the mercury in the eudiometer was so adjusted that when the pressure tube was opened, the mercury in it would stand near one of the Jolly points. Then the level of the reading microscope was adjusted, and the meniscus was brought into focus. During this time, the water surrounding the eudiometer was stirred by a current of air. When everything was ready the current of air was shut off, and the piston valve slowly moved till the mercury exactly coincided with the Jolly point. Then, within five or ten seconds, the thermometer was read and the fraction of a millimetre shown in the reading microscope was determined. The water was then again stirred, the adjustment at the Jolly point, and the reading of the thermometer and of the reading microscope was repeated. By means of the fine adjustment of the level of the mercury which has been mentioned, the adjustment at the Jolly point could be made within the 500th of a millimetre, and it could be repeated as many times as was desired. It was also possible to make the final adjustments, and the two readings, within a time too short for any change of temperature in the gas to be measured. Readings of temperature were to the two-hundredth of a degree, and of level to the two-hundredth of a millimetre. To show what degree of accuracy can be obtained by an apparatus such as is here described, including both errors of readings and errors of transfer due to bubbles of gas entangled in the capillary tube, I put a quantity of gas in a jar in the cistern, transferred it to the eudiometer and measured it, transferred it back to the jar and measured it again, and so ten times. I give the reduced volumes so found. From this it seems that the probable error of measurement, not including errors of calibration, are something like a 70,000th part of volumes like those used in the determinations of the volumetric composition of water. I also found the mean error of a single measurement by computation from the mean error of a determination of the ratio sought. In this way it seems that the mean error of a single measurement of such a volume as 150 or 200 c.c. is its 50,000th part. This value includes the errors of calibration as far as they affect a determination of the ratio. The direct determination of mean error of measurement was made under selected conditions as to illumination and health which could not be secured in the determinations of the ratio.

Repeated Measurements of the same Volume of Gas transferred to Jar after each Measurement.

210.81 c.c.	210.805 c.c.
210.815 "	210.815 "
210.815 "	210.81 "
210.815 "	210.81 "
210.815 "	210.81 "

(To be continued).

AN APPARATUS FOR HEATING SUBSTANCES IN GLASS TUBES UNDER PRESSURE.*

By H. PEMBERTON, Jun.

CHEMISTS who do not happen to have in their laboratories oil or air baths for heating closed tubes can make an air bath at short notice from materials furnished by all dealers in steam fittings.

Order:—

(1) One four-inch wrought-iron pipe, eighteen inches out to out, with usual thread on each end. At about nine inches from either end this pipe is drilled and tapped for a one-inch nipple in such a manner that a pipe introduced would pass, not on a line with the radius, but about half-way between the axis of the four-inch pipe and its walls; in other words, it would be on a line with a chord of the circle.

(2) One one-inch wrought-iron nipple, two inches long, one-inch thread on one end.

(3) Two four-inch malleable iron caps, drilled and tapped for a one-inch pipe.

(4) One one-inch wrought-iron pipe, twenty-four inches out to out, with a three-inch straight thread on each end.

(5) Two one-inch iron caps. A hole, one-eighth of an inch in diameter, is drilled in the end of one of these caps.

The above order can be given *literatim*, and will be understood by the dealer, who will furnish, at a trifling cost, the materials, cut and tapped as ordered.

Fig. 1 shows how the whole is put together. The numbers on the figure correspond also to the numbers of the paragraphs of the order as given above.

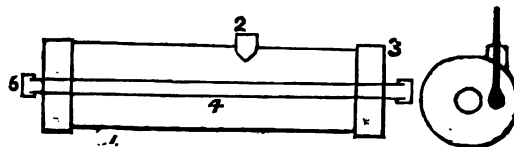


FIG. 1.

FIG. 2.

Fig. 2 is an end section. A cork is inserted in 2, and through it a thermometer, the bulb of which is on a level with the interior pipe. The whole is supported on a few bricks at either end, and is kept steady and in place by a couple of weights or half bricks. It is heated by one or two Bunsen burners, according to the temperature desired.

Determination of Actual Glycerin in Crude Glycerins.—F. Filsinger (*Chem. Zeit.*), continuing his controversy with Lewkowitsch, has again examined a number of samples of glycerin both by the permanganate method and by the acetin process. The results of the latter are too high and mutually discordant.

Quantitative Determination of Paraffin especially in Mineral Oils.—R. Zoloziecki (*Dingler's Polyt. Jour.*).—The author dissolves the paraffin in amyl alcohol and precipitates it with ethylic alcohol. 10—20 c.c. or grms. of the sample are mixed with 5 parts of amyl alcohol, and then with the same quantity of ethylic alcohol at 75° Tr. The mixture is let stand for some hours in a cold place (if possible not above 4°), filtered through a dry, cold filter, and the residue is washed on the filter with a cooled mixture of 2 parts amyl alcohol and 1 part ethylic alcohol at 70°. The deposit dried in the air is exhausted on the filter with ether or benzine in a suitable apparatus, the solvent evaporated, the residue dried at 125° for two hours, and weighed. The method cannot be used for examining wax, as it contains constituents precipitable by alcohol.

* Read at the Chemical Section of the Franklin Institute, March 17, 1891.

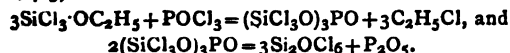
ON THE ACTION OF
PHOSPHORUS OXYCHLORIDE ON THE
ETHERS AND CHLORHYDRINES OF SILICIC
ACID.*

By H. N. STOKES.

THAT silica can combine with other acids, forming mixed anhydrides, has long been known, and several such bodies have been described. Friedel and Ladenburg (*Ann. Chem. (Liebig)*, cxlvi., 174) obtained the tetra-acetyl derivative $\text{Si}(\text{O} \cdot \text{CO} \cdot \text{CH}_3)_4$ by treating silicon tetrachloride with acetic acid or anhydride. Friedel and Crafts (*Ann. Chim. Phys.* [4], ix., 47) obtained $\text{Si}(\text{OC}_2\text{H}_5)_3\text{O} \cdot \text{CO} \cdot \text{CH}_3$ from ethyl orthosilicate and acetic anhydride. Hautefeuille and Margottet (*Compt. Rend.*, xcvi., 1052) described a crystalline compound, $\text{SiO}_2 \cdot \text{P}_2\text{O}_5$, formed by fusing amorphous silica with metaphosphoric acid.

By the action of phosphorus oxychloride on silicic ethers and their chlorine derivatives, I have obtained bodies which consist of phosphoryl chlorides in which the chlorine is partly replaced by a residue of silicic acid, and which are therefore chlorides of silicophosphoric acids.

Phosphorus oxychloride was caused to react upon orthosilicic ethyltrichlorhydrine, $\text{SiCl}_3 \cdot \text{OC}_2\text{H}_5$, hoping thereby to obtain the silicon oxychloride described by Friedel and Ladenburg (*Liebig's Ann. Chem.*, cxlvii., 355) and by Troost and Hautefeuille (*Ann. Chim. Phys.* [5], vii., 465):—



The experiment proved that this reaction does not take place.

If the trichlorhydrine be heated in a sealed tube with an excess of phosphorus oxychloride, no reaction is apparent below 175° , the contents remaining perfectly clear. If the temperature be kept at 180° — 200° , a white amorphous substance is soon formed which is sufficiently porous to absorb all the liquid products. After two to three hours' heating the tube is opened, when ethyl chloride escapes in large quantities. On placing the tube in an air-bath heated at about 150° , and connecting it with a condenser, a large amount of liquid may be collected. The solid remaining in the tube may then be freed from excess of phosphorus oxychloride by passing a current of dry air over it by means of a capillary.

The liquid, on fractionating, is readily separated into phosphorus oxychloride (boiling at 110°) and silicon tetrachloride (boiling at 57° — 61°), though much of the latter is lost, being carried off by the ethyl chloride which is abundantly held in solution. The product obtained after six distillations was analysed.

	Calculated for SiCl_4 .	Found.
Si	16.52	16.24

The view with regard to its nature was confirmed by converting it into ethyl orthosilicate (boiling at 165.5°). As the liquid passed over entirely below 112° , no silicon oxychloride was formed, and no substances other than those mentioned could be detected.

Analyses of the solid substance gave:—

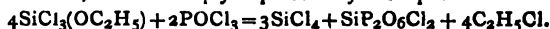
	Calculated for $\text{SiP}_2\text{O}_6\text{Cl}_4$.	Found.	
		I.	II.
Si	10.92	10.17	10.06
P	24.15	25.16	25.11
Cl	27.59	27.33	—

The agreement is only approximate, as the substance could not be purified in any way; and on heating too long or at too high a temperature when drying, phosphorus

oxychloride is slowly given off. It is possibly a mixture of substances, in the formation of which the one supposed represents one stage. If heated above 200° phosphorus oxychloride is given off, and, at a red heat, phosphorus pentoxide; and the residue left at a white heat consists of amorphous silica imbedded in a vitreous substance, probably the compound $\text{SiC}_2 \cdot \text{P}_2\text{O}_5$ of Hautefeuille and Margottet. The loss on heating corresponds to the equation $6\text{SiP}_2\text{O}_6\text{Cl}_4 = 3\text{SiO}_2 + 3(\text{SiO}_2 \cdot \text{P}_2\text{O}_5) + 4\text{POCl}_3 + \text{P}_2\text{O}_5$.

	Calculated.	Found.
Loss	49.01	51.86

The formation of the substance, which, for reasons given below, may be designated as *silicopyrophosphoryl chloride*, is most simply expressed by the equation—



Silicopyrophosphoryl chloride is a very bulky substance, resembling the lightest form of amorphous silica. It may be obtained perfectly colourless, but is usually more or less coloured by organic matter, formed by secondary reactions, when heated too high. It is extremely hygroscopic, and gives off hydrochloric acid instantly when exposed to moist air. It is readily soluble in absolute alcohol—a proof that it contains no free silica. The alcoholic solution, which probably contains an ether of silicophosphoric acid, may be evaporated nearly to dryness, or heated any length of time at 150° without decomposition. On heating at 225° it soon deposits transparent gelatinous silica. The solution in alcohol is attended with considerable rise of temperature. The substance is insoluble in ether. If cold water be poured on the fine powder it readily dissolves, with the exception of a few flakes of silica; but if first moistened, or if in lumps, most of the silica remains undissolved: the best way to get a clear aqueous solution is to dissolve in a little alcohol and then to dilute with water. The reaction with water alone is somewhat violent. The aqueous solution may be kept a long time—indeed, may be strongly concentrated on the water-bath—but on evaporation to dryness a vitreous mass is left, from which water extracts phosphoric acid only.

All attempts to prepare salts of silicophosphoric acid have failed. Ammonium carbonate precipitates gelatinous silica. If the cold aqueous solution, prepared as described above, be acidified with nitric acid, excess of silver nitrate added, and filtered from silver chloride, a clear solution is obtained. If to this be added, drop by drop, dilute ammonia, a white precipitate is formed, which at a certain point changes to yellow. The analysis of the white substance (dried at 100°) gave—

	Calculated for $\text{Ag}_4\text{P}_2\text{O}_7$.	Found.
Ag	71.17	71.25

The yellow precipitate proved to be merely silver orthophosphate.* The filtrate from the silver salts gives an abundant precipitate of silicic acid when warmed with ammonia. The magnesia precipitate also shows the characteristic reaction of magnesium pyrophosphate, dissolving in acetic acid when precipitated in the cold, and being re-precipitated from this solution on boiling.

The substance is therefore a derivative of pyrophosphoric acid, and the formation of some orthophosphoric acid may be explained by the decomposition of the former—pyrophosphoryl chloride dissolving in water with forma-

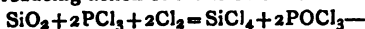
* The reaction described above affords a convenient method for separating, at least approximately, ortho- from pyrophosphoric acid. A solution of the acids—or their soluble salts—is acidified in the cold with nitric acid, and silver nitrate added in excess. On adding dilute ammonia, drop by drop, all the pyrophosphoric acid is precipitated before any of the orthophosphoric acid comes down. At this point a single drop of ammonia gives a yellow tinge to the precipitate, which a drop of dilute nitric acid causes to disappear. If the liquid be now filtered, all the pyrophosphoric acid will be in the precipitate and all the orthophosphoric acid in the filtrate. The reaction is so sharp that it might possibly be used to separate the acids quantitatively.

tion of orthophosphoric acid (Michaelis, *Ber. d. Chem. Ges.*, iv., 767).

Heated with phosphorus pentachloride at 100°, silico-pyrophosphoryl chloride is readily and quantitatively converted into silicon tetrachloride and phosphorus oxychloride, $\text{SiP}_2\text{O}_6\text{Cl}_2 + 4\text{PCl}_5 = \text{SiCl}_4 + 6\text{POCl}_3$.

The tetrachloride was isolated, and expectations with regard to its nature were confirmed on converting it into the ether (b. p., 165.5°). No silicon oxychloride could be obtained. If heated with an insufficient amount of phosphorus pentachloride, the excess remains apparently unchanged.

The conversion of a derivative of silicic acid into silicon tetrachloride at so low a temperature has not been hitherto observed. R. Weber (*Ann. der Phys. Pogg.*, cxii., 619) obtained the tetrachloride and phosphorus oxychloride by passing the vapour of phosphorus pentachloride over silica at a red heat. As the pentachloride is completely dissociated at 300° into trichloride and chlorine, the reaction is due to the action of chlorine, combined with the reducing action of the trichloride—



which is analogous to the old method of preparing the tetrachloride, $\text{SiO}_2 + 2\text{C} + 2\text{Cl}_2 = \text{SiCl}_4 + 2\text{CO}$.

As I have convinced myself, phosphorus pentachloride does not act on amorphous silica (dried at 100°), even at 250°, further than to dehydrate it.

The action of a smaller quantity of phosphorus oxychloride on the trichlorhydrine is similar. 3 mols. trichlorhydrine and 1 mol. oxychloride, heated at 180°, gave ethyl chloride, silicon tetrachloride, and a solid product completely soluble in alcohol and water, the composition of which differed, however, from that of the substance above described. (Found: Si, 15.25; P, 22.30; Cl, 14.13).

The action of an excess of phosphorus oxychloride on the chlorhydrines $\text{SiCl}_2(\text{OC}_2\text{H}_5)_2$ and $(\text{SiCl}(\text{OC}_2\text{H}_5)_3)_2$ is essentially similar. At 180–200° a solid substance is formed, with much ethyl chloride and silicon tetrachloride. The amount of the tetrachloride is directly, and that of the solid inversely proportional to the amount of chlorine in the chlorhydrine. In each case the tetrachloride was isolated in a state of approximate purity, and converted into the ortho ether, boiling at 165.5°. No other volatile substances could be detected. The solid body was completely soluble in alcohol, and, in brief, showed all the properties above described as belonging to silico-pyrophosphoryl chloride.

The analysis of the product from $\text{SiCl}_2(\text{OC}_2\text{H}_5)_2$ gave—

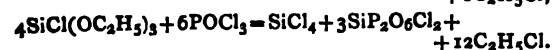
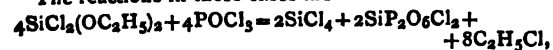
	Calculated for $\text{SiP}_2\text{O}_6\text{Cl}_2$.	Found.	
		I.	II.
Si ..	10.92	11.68	11.80
P ..	24.15	24.53	24.91

The product from $\text{SiCl}(\text{OC}_2\text{H}_5)_3$ gave—

	Calculated for $\text{SiP}_2\text{O}_6\text{Cl}_2$.	Found.
Si ..	10.92	10.15
P ..	24.15	24.54
Cl ..	27.59	24.73

The results, as before, are only approximate; but, it must be remembered, the body loses phosphorus oxychloride slowly on heating, and only the crude product could be analysed.

The reactions in these cases are—



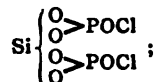
Orthosilicic ether, $\text{Si}(\text{OC}_2\text{H}_5)_4$, was heated with excess of phosphorus oxychloride for two hours at 180–200°. The tubes contained a solid substance and ethyl chloride. On distilling off the excess of oxychloride and decomposing it with water, only a trace of silica was left after evapora-

tion, showing that practically no volatile silicon compound was formed. The solid, the properties of which were in every respect identical with those of the body above described, gave on analysis—

	Calculated for $\text{SiP}_2\text{O}_6\text{Cl}_2$.	Found.		
		I.	II.	III.
Si ..	10.92	9.92	10.05	10.21
P ..	24.15	25.52	25.63	25.84
Cl ..	27.59	29.66	29.90	—

The reaction is, therefore, represented by the equation, $\text{Si}(\text{OC}_2\text{H}_5)_4 + 2\text{POCl}_3 = \text{SiP}_2\text{O}_6\text{Cl}_2 + 4\text{C}_2\text{H}_5\text{Cl}$.

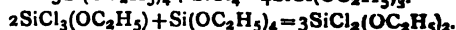
The constitution of the silico-phosphoryl chloride is possibly very complex. The simplest constitutional formula, deduced from the last equation, would be—



but as this would give no pyro-phosphoric acid on decomposition with water, we must assume that it is—



or a polymer containing the group $-\text{O} \cdot \text{PO} \cdot \text{O} \cdot \text{PO} \cdot \text{O}-$, which makes it a derivative of metasilicic acid. The cause of the formation of silicon tetrachloride from the chlorhydrines is not clear. It is obviously not due to a direct replacement of ethoxyl by chlorine, for then it should be obtained in the same amount from each chlorhydrine or from the ether; whereas the latter does not give it, and the amount obtained from the former is proportional to the amount of chlorine they already contain. Besides, no phosphoric ethers are formed. Nor does the supposition explain the formation of silico-pyrophosphoryl chloride in quantities inversely as the amount of chlorine. A possible explanation is the following:—The chlorhydrines* are formed by heating mixtures of orthosilicic ether with silicon tetrachloride, or of either of these with other chlorhydrines, that one being formed in largest amount which corresponds in composition to the mean composition of the mixture; for example—



These reactions take place below 200°, partial dissociation occurring, the products re-uniting to form that body which tends to give the liquid a homogeneous composition. Doubtless the reverse process takes place at the same time; for example—



and if phosphorus oxychloride be present—which, as just shown, destroys the ether—this can go on until all the chlorhydrine has been converted into ether and tetrachloride. This explanation is simple enough, but, as shown by the action of phosphorus oxychloride on *disilicic* chlorhydrines, the actual process is possibly more complicated.

By heating a mixture of trichlorhydrine, phosphorus, and iodine, a solid of similar properties was obtained, and silicon tetrachloride was formed. The reaction was not followed further.

Action of Phosphorus Oxychloride on Derivatives of Disilicic Acid.

Hexethyl disilicate, $\text{O} < \begin{matrix} \text{Si}(\text{OC}_2\text{H}_5)_3 \\ \text{Si}(\text{OC}_2\text{H}_5)_3 \end{matrix}$, was heated with an excess of phosphorus oxychloride in sealed tubes at 180–200° for two or three hours. The tubes contained a white solid, outwardly resembling silico-pyrophosphoryl chloride and much ethyl chloride. No volatile silica

* Friedel and Crafts, *Ann. Chim. Phys.*, [4] ix., 12, 13, 15.

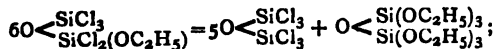
† *Ibid.*, [4] ix., 24.

compound was formed. The solid resembled in its general properties the one described. It was completely soluble in alcohol, and therefore contained no free silica. The solution gave the reactions of pyro-phosphoric acid. It differed markedly in composition from the ortho-silicic derivative, the analysis giving—

	Calculated for SiP ₂ O ₆ Cl ₂ .	Found.
Si	10.92	17.03
P	24.15	23.91
Cl	27.59	21.04

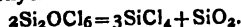
This corresponds to no probable formula, but contains 4 atoms Si to 5 atoms P, instead of 1 atom Si to 2 atoms P. Phosphorus pentachloride converts it readily (at 100°) into silicon tetrachloride and phosphorus oxychloride. No silicon oxychloride is formed, the product passing over entirely below 112°. The tetrachloride was isolated and converted into the tetrethyl ether (boiling at 165.5°).

The ease with which the ortho-chlorhydrines give, with phosphorus oxychloride, silicon tetrachloride, led to an analogous experiment with the *disilicic chlorhydrines*, in the hope that in this way silicon oxychloride might be obtained. On the above hypothesis, we should have, in the presence of phosphorus oxychloride, the following reaction:—



and analogous reactions with the other chlorhydrines.

The disilicic chlorhydrines, which have not hitherto been prepared, are formed by heating disilicic ether with an excess of silicon tetrachloride for several hours at 200°. A gradual exchange of ethoxyl and chlorine occurs, disilicic chlorhydrines and orthosilicic trichlorhydrate being formed. After distilling off the latter, the residue is again heated with silicon tetrachloride, whereby the conversion is carried further. In this way a mixture of disilicic chlorhydrines was obtained, which, after freeing from all orthosilicic compounds by repeated distillation, boiled at 170–220°. A chlorine determination showed that it contained the equivalent of 65 per cent Si₂OCl₆. No attempt was made to isolate any of these chlorhydrines, as no less than eight are theoretically possible, and it was presumed that they would all act in the same way toward phosphorus oxychloride. The mixture was heated with excess of phosphorus oxychloride (based on the amount of chlorine shown by analysis), for 2½ hours at 180–200°; after which no further action was observed. The appearance of the product was the same as in previous experiments. The liquid product was distilled off and fractionated. It was found to consist of an excess of phosphorus oxychloride, of *silicon tetrachloride*, which was recognised through conversion into the ether, and ethylchloride. The liquid boiled entirely below 112°, and therefore none of the expected silicon oxychloride was formed. The solid product was markedly different from those before obtained. It was only partly soluble in alcohol, and on boiling out with the solvent, a large residue of *silica* was left. Besides a soluble silico-phosphoryl chloride and ethyl chloride, the only products were silicon tetrachloride and silica. If the oxychloride be formed at all, it is at once decomposed in the presence of phosphorus oxychloride—



Whether this actually occurs is questionable, as the oxychloride and all the other substances concerned are, by themselves, stable at a very much higher temperature than that employed. I am unable to give any satisfactory explanation of the reaction.

Amorphous silica, prepared from water-glass and dried at 200°, gives with phosphorus oxychloride a small amount of silicophosphoryl chloride, soluble in alcohol: 3.5 per cent of the silica was converted into this compound.

The silicon tetrachloride used as the starting material of these experiments was made by the admirable method

of Gattermann (*Ber. d. Chem. Ges.*, xxii., 186-8). For preparing the silicon mixture I used, instead of test-tubes, sheet-iron crucibles of about 200 c.c. capacity. These are nearly filled with an intimate mixture of three parts quartz powder and one part magnesium powder, tightly pressed down. On heating over a blast lamp, the reaction starts in a few seconds, and is indicated by the whole crucible suddenly becoming red-hot. During the reaction the lid must be held down firmly. I prefer to extract the magnesia from this product before using it, as less care has to be used in regard to temperature when passing chlorine over it. By using ice alone, to condense the chloride, nearly the theoretical yield is obtained: the crude product loses about 15 per cent in the process of purification.

The *orthochlorhydrines* were prepared essentially according to the method of Friedel and Crafts (*loc cit.*). Any mixture may be used which coincides in composition with that of the chlorhydrate desired. The yield is never theoretical, no matter how long the heating may be continued. The yields of pure substance, obtained after six distillations, were as follows:—Monochlorhydrate, 65 per cent; dichlorhydrate, 40 per cent; trichlorhydrate, 47 per cent. More can, of course, be obtained by uniting and heating the residues.

Friedel and Crafts (*Ann. Chim. Phys.*, [4], ix., 26) obtained the disilicic ether by adding to silicon tetrachloride, drop by drop, alcohol containing the calculated amount of water. They claim that the yield is nearly theoretical. I am not able to confirm this statement. By following their directions exactly, I obtained a mixture of ortho and disilicic ethers, with ethers of much higher boiling-points. After repeated fractioning, only 33 per cent of the theoretical yield of disilicic ether was obtained, and the amount of ortho-ether was much greater. This is due to the fact that the added water acts on the disilicic ether already formed, giving more complex bodies, so that there is an excess of tetrachloride, which is converted into ortho-ether.

The essential results of these experiments may be summed up as follows:—

Phosphorus oxychloride acts on orthosilicic ether and its chlorine derivatives according to the following equations:—

- I. $4\text{Si}(\text{OC}_2\text{H}_5)_4 + 8\text{POCl}_3 = 4\text{SiP}_2\text{O}_6\text{Cl}_2 + 16\text{C}_2\text{H}_5\text{Cl}.$
- II. $4\text{SiCl}(\text{OC}_2\text{H}_5)_3 + 6\text{POCl}_3 = \text{SiCl}_4 + 3\text{SiP}_2\text{O}_6\text{Cl}_2 + 12\text{C}_2\text{H}_5\text{Cl}.$
- III. $4\text{SiCl}_2(\text{OC}_2\text{H}_5)_2 + 4\text{POCl}_3 = 2\text{SiCl}_4 + 2\text{SiP}_2\text{O}_6\text{Cl}_2 + 8\text{C}_2\text{H}_5\text{Cl}.$
- IV. $4\text{SiCl}_3(\text{OC}_2\text{H}_5) + 2\text{POCl}_3 = 3\text{SiCl}_4 + \text{SiP}_2\text{O}_6\text{Cl}_2 + 4\text{C}_2\text{H}_5\text{Cl}.$

The body SiP₂O₆Cl₂ is the chloride of a silico-pyrophosphoric acid, is decomposed by water into silica and pyrophosphoric acid, and is easily converted by phosphorus pentachloride into silicon tetrachloride and phosphorus oxychloride.

The ether of disilicic acid acts similarly, giving a silico-phosphoryl chloride of different composition but analogous properties.

The chlorhydrines of disilicic acid do not give with phosphorus oxychloride, as might be inferred, a silico-phosphoryl chloride and silicon oxychloride, but a mixture of the first with free silica and silicon tetrachloride.

Phosphorus trichloride also acts on orthosilicic ether at 200°, giving a white solid, and liquid products, which will be further studied.

In conclusion, I wish to express my indebtedness to Prof. F. W. Clarke for liberally placing at my disposal the means of carrying out these experiments.

The Atomic Weight of Bismuth.—Alex. Classen (*Ber. Deutsch. Chem. Gesell.*).—If we take O=16 the author finds Bi=208.918; if we assume O=15.96 Bi=208.396.

NOTICES OF BOOKS.

A Dictionary of Applied Chemistry. By T. E. THORPE, B.Sc. (Vict.), Ph.D., F.R.S., Treasurer C.S., Professor of Chemistry in the Royal College of Science, London. In Three Volumes. Vol II. London and New York: Longmans, Green, and Co.

AMONG the more elaborate articles in this volume must be mentioned those on "Evaporation" and on "Explosives." The latter subject is becoming increasingly complicated from the number of patented and secret compounds and the perplexed synonymy.

"Extraction Apparatus" forms the subject of a thorough-going and well-illustrated article.

The chapter on Fermentation naturally includes a careful study of bacteria or schizomycetes.

In the article on "Filtration" we find a remark which does not agree with our experience. The writer says:—"There are precipitates which instead of forming a bed through which the liquid can percolate form a gelatinous layer over the filtering surface practically impervious to water. As an example, precipitated sewage sludge, to which insufficient lime has been added, may be taken." We have proved, on the contrary, that sewage sludge is capable of filtration in the total absence of lime.

Under water-gas we do not find any caution as to its poisonous character, though analyses quoted show the presence of carbon monoxide in proportions up to 43 per cent. The conclusion is expressed that water-gas, whose actual heating-power is to that of coal-gas only as 2 to 5, cannot compete with the latter, even if it could be produced at the works for nothing.

The article on Lakes is fairly exhaustive, and is ably written.

General Chemical Mineralogy. (Allgemeine Chemische Mineralogie). By Dr. C. DOELTER. Leipzig: Engelmann (8vo., pp. 227).

THIS useful little work, after an introduction expounding general chemical principles, discusses crystallo-chemistry, including dimorphism, physical and chemical isomerism, enanti-tropismism, monotropism, isomorphism, and isodimorphism.

We then come to the chemical analysis of minerals in the dry and the wet way; mineral synthesis is next considered. For the products of this process the author prefers the name artificial minerals. He distinguishes between chemical and mineralogical synthesis, the object of the former being merely the production of a compound which agrees with the natural mineral in its chemical attributes, whilst a mineralogical synthesis to be successful must reproduce the product morphologically and physically as well as chemically.

In a chapter on the formation of minerals in nature there are some interesting remarks on the production of minerals by electric currents and by organisms. The decomposing action of plants does not seem to fall within the author's plan.

The last chapter of the work deals with the chemical composition and constitution of minerals.

At the end of the book we find a good index of the authors quoted, in which very few British names occur, a supplement, and an explanation to the fourteen figures.

Students of mineralogy—a subject the popularity of which is far from being on a level with its importance—will find Dr. Doelter's work a valuable guide.

On the Preparation and the Reaction of Ammonium-Mercury Chlorides.—G. André.—Not suitable for abstraction, and not sufficiently important for reproduction in full.—*Comptes Rendus*, cxii., No. 16.

CORRESPONDENCE.

THE COMPOSITION OF WATER.

To the Editor of the Chemical News.

SIR,—I have read with much interest Mr. Morley's account of his experiment on the "Composition of Water," but is there not some mistake in his estimate of the power required to decompose the water? I have always understood that the quantity of water decomposed by a current of electricity was a measure of the quantity of electricity passing through the cell; yet Mr. Morley obtains the same amount of gas with two currents, one thirty times as strong as the other. This surely must be wrong. Of course if the current strength did not alter by increasing the number of voltmeters, then the amount of gas evolved in each cell would be the same as if only one were used, but the addition of each voltmeter increases the resistance, and consequently the current must be proportionately reduced.—I am, &c.,

W. A. R.

Plymouth, May 10.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxii., No. 16, April 20, 1891.

On Certain Calorimetric Data.—M. Berthelot.—Not available for useful abstraction.

On the Crystalline Form and the Optical Properties of the New Crystalline Variety of Sulphur of M. Engel.—C. Friedel.—M. Engel's sulphur, independently of its physical and chemical properties, is completely differentiated from all known varieties of crystalline sulphur by its crystalline form.

Dissociation of Amylene Hydrobromate at Low Pressures.—G. Lemoine.—The author's conclusions are shown by the graphic method.

On the Salts of Argentous Oxide.—M. Güntz.—The author has recently shown the existence of a perfectly definite crystalline salt, Ag_2F . By setting out from this product it is easy to obtain the other argentous salts. He has prepared Ag_2Cl , Ag_2S , and Ag_2I .

On Boron Sulphide.—Paul Sabatier.—The author prepares boron sulphide by the action of hydrogen sulphide upon amorphous boron heated to redness. The reaction begins near the temperature at which glass softens and is not complete.

On Hydrogen Boride.—Paul Sabatier.—The hydrogen boride of Jones seems to consist of hydrogen containing a very small quantity of boron hydride. This compound is an exceedingly offensive gas, which burns with a splendid green flame, and is resolved at a red heat into its elements.

On Two New States of Sulphur.—M. Engel.—This paper does not admit of useful abridgment.

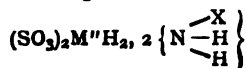
Action of Urea upon Sulphanilic Acid.—J. Ville.—The author has obtained a sulphanilic carbamic acid—



Determination of Acetone in Denaturated Alcohols.—Leo Vignon.—The acetone may be determined in such alcohols by conversion into iodoform. Iodine must be used in very large excess. The details of the operation may be found in *Comptes Rendus*, cx., p. 534.

The author is studying the form in which sulphanic acid is eliminated from the animal economy.

New Compounds obtained with Metallic Sulphites and Aromatic Amines.—G. Denigès.—The compounds obtained answer to the general formula—



in which M'' is a bivalent metal (such as Cd, Mn, Fe, Co, or Ni), and X is an aromatic nucleus.

Purification of Industrial Waste Waters and Sewage.—A. and P. Buisine.—The authors venture on the statement that ferric sulphate has not been much used hitherto in the treatment of sewage in default of an economical method for its preparation. They sprinkle burnt pyrites with sulphuric acid at 66° B.

Zeitschrift für Analytische Chemie.

Vol. xxix., Part 4.

Determination of Tannic Acid in Tanning Materials.—F. Gantter, R. Procter, and E. Guenez.—The former part of this paper will be given in full. The researches of R. Procter will be found in the *Journ. Soc. Chem. Ind.*, and those of E. Guenez have been noticed under the *Comptes Rendus*.

Quantitative Determination of Citric Acid in Vegetable Matter.—Edo Claassen (*Pharm. Rundschau und Chemiker Zeitung*).—The plants, &c., are extracted with a very dilute solution of ammonia and ammonium carbonate slightly concentrated, precipitated with lead acetate and filtered. The dry precipitate is extracted at a boil with strong alcohol, suspended in water, treated with sulphuretted hydrogen to remove the lead and filtered. The filtrate is evaporated down to a thin syrup mixed with ammonium chloride, excess of ammonia and calcium chloride, and three times the volume of ammonia is added. The precipitate which is formed is filtered off, washed with a mixture of 3 parts alcohol and 1 part water, and after expelling the alcohol by evaporation to dryness, it is dissolved in hot hydrochloric acid, largely diluted. When cold it is filtered, the filtrate is mixed with an excess of ammonia and filtered again. The filtrate is then evaporated to dryness on the water-bath, the residue is taken up with boiling ammoniacal water, and the precipitate, calcium citrate, is collected on a weighed filter and washed with hot water. As a precaution the filtrate thus obtained is again evaporated to dryness and treated as above, in order to collect further small quantities of calcium citrate which are also collected upon a tared filter.

Methods for the Determination of Starch.—W. Lenz.—This paper will be inserted in full if possible.

Determination of the Diastatic Value of Extracts of Malt.—R. A. Cripps.—From the *Pharm. Journ. and Transactions*.

The Impurities of Salicylic Acid.—B. Fischer (*Pharm. Zeit.*).—The chief impurities in salicylic acid are cresotic acid, paraoxybenzoic acid, and oxyisophthalic acid. B. Fischer recommends the following simplified process:—3 grms. salicylic acid are added to 200 c.c. boiling water holding in suspension 1–2 grm. pure calcium carbonate. After the reaction has taken place the liquid is boiled down to 5 c.c. over a free flame, so that there is a plentiful separation of crystals even whilst hot. When cold the mother-liquor and the washings are boiled down to about 1 c.c. in a wide test-tube, and induced to crystallise by rubbing with a glass rod. It is diluted with 1 c.c. of water, filtered through wadding, and again concentrated to 1 c.c. From this liquid hydrochloric acid (if the sample contains 3–5 per cent of the cresotic acids), throws down an acid mixture which melts underneath hot water and collects at the bottom of the tube as a

thick, oily drop. Acids containing 0.5 to 1 per cent of cresotic acid do not display this phenomenon. For separating salicylic acid from α -oxyisophthalic acid the mixture must be submitted to distillation along with steam. The non-volatile oxyisophthalic acid remains behind as a light grey powder, and may be shaken out with ether. It is then obtained in snow-white needles by solution in excess of hydrochloric acid and filtration through charcoal. These acicular crystals resemble salicylic acid, but melt with decomposition at 300–305°. The acid is very sparingly soluble in water, easily in alcohol, less readily in ether. It is precipitated by an excess of baryta; the silver salt is sparingly soluble. On separation by calcium salts it remains in the last filtrate.

Determination of Petroleum in Oil of Turpentine.—W. M. Burton.—From the *American Chemical Journal*.

The Examination of Gas Coke.—L. T. Wright (*Society of Chemical Industry*).

Sophistication of Indian Castor Oil with Cocoa-Nut Oil.—M. Conroy.—From the *Pharm. Journ.*

Determination of Morphine in Opium and its Extracts.—A long series of notices from the *Pharm. Central Halle*, the *Archiv. der Pharmacie*, the *American Apotheker Zeitung*, the *American Chemical Journal*, the *Moniteur Scientifique*, &c.

Alkaloidal Reactions of Cubebine.—E. Schär (*Archiv. der Pharmacie*).—For this paper we must refer to the original.

Re-determination of the Atomic Weight of Gold.—J. W. Mallet.—From the *Phil. Trans.* The author concludes in favour of the value 196.762.

Moniteur Scientifique, Queneville.

Series 4, Vol. iv., Part 2, No. 535.

Eugène Peligot.—Aimé Girard.—A discourse in memoriam delivered at the Annual Meeting of the Société d'Encouragement.

Detection of Impurities Present in Alcohol.—Ed. Mohler.—An examination of the behaviour of the various alcohols, aldehyde, and ethers present in commercial alcohol according to the colouration which it takes on treatment in heat with sulphuric acid, the colour developed by the action of rosaniline bisulphite, the detection of furfural by means of aniline acetate, and reduction with potassium permanganate.

The Reactions of Red Prussiate (Potassium Ferricyanide).—M. Prud'homme.—The author examines the action of solutions of ferricyanide with metals and oxides—that of lead nitrate, the ferricyanide, the respective reactions of ferricyanide and potassium chlorate, chromate, and nitro prussiate.

On Bees' Wax.—A. and P. Buisine.—The first portion of an extensive treatise.

Studies on the Tanning Woods.—S. S. Arnaudon.—An account of tanning materials belonging to the family of the Anacardiaceæ, such as the species of *Astronium* or *Urundey*, *Lythcea* or *Molle*, *Schinopsis Laentzii* or *Quebracho*—all natives of South America.

Influence of Silicon upon the Properties of Steel.—R. A. Hadfield.—From the *CHEMICAL NEWS*.

On Nickel Steel.—J. Hopkinson.—From the *Proc. Roy. Soc.*

Presence of Iron in Zinc obtained from the Dust of Blast Furnaces.—E. Jensch.—The mean proportion of iron present was 22.96 FeO. The finer the dust the more ferrous oxide it contained.

The Obstruction of Gas-Pipes by Naphthalene, and on the Products of the Dry Distillation of Different Coals.—Watson Smith, F.C.S.—From the *Journ. Soc. Chem. Ind.*

MISCELLANEOUS.

Royal Institution.—Dr. A. C. Mackenzie, Principal of the Royal Academy of Music, will, on Thursday next (May 21st), begin a course of four lectures on "The Orchestra, considered in connection with the Development of the Overture"; and Professor A. H. Church, Professor of Chemistry in the Royal Academy of Arts, will, on Saturday (May 30th), begin a course of three lectures on "The Scientific Study of Decorative Colour."

Detection of Colchicine in Human Remains.—N. Obolonski (*Vierteljahresschrift für Gerichtliche Medicin und öffentl. Sanitätswesen*).—The intestines, &c., are ground up with glass-powder, the mass is mixed with oxalic acid and digested for 12 hours with alcohol. The liquid is pressed, the dry residue washed twice with alcohol and pressed again. The alcoholic liquids are concentrated on the water-bath at a temperature not exceeding 80°, the cooled residue is again taken up with alcohol to its original volume, filtered, the filtrate concentrated at a gentle heat, the residue re-dissolved, and the filtrate concentrated. These operations are repeated three times, the alcohol is evaporated off, the residue taken up in water, the solution purified by shaking out with petroleum ether, and the colchicine is finally obtained by shaking out with chloroform. In order to distinguish the alkaloid when separated, the author uses the violet colouration with nitric acid, also Erdmann's reagent (nitrosulphuric acid), which gives first a green colour, then deep blue, violet, and yellow, turning raspberry-red on the addition of an alkali, and also Mandelin's test (1 part ammonia vanadate in 200 parts sulphuric acid), which gives a green colour. Colchicine is not readily decomposed on putrefaction. It is most readily found in the kidneys, bladder, and urine.

MEETINGS FOR THE WEEK.

- TUESDAY, 19th.**—Pathological, 8.30 (Anniversary).
Royal Institution, 3. "The Betterton Period of Stage History," by William Archer.
- WEDNESDAY, 20th.**—Meteorological, 7.
Microscopical, 8.
Pharmaceutical, 11 a.m. (Anniversary).
- THURSDAY, 21st.**—Chemical, 8.
Institute of Electrical Engineers, 8.
Royal Institution, 3. "The Orchestra considered in connection with the Development of the Overture," by A. C. Mackenzie, Mus. Doc.
- FRIDAY, 22nd.**—Royal Institution, 9. "The Molecular Process in Magnetic Induction," by Prof. J. A. Ewing, M.A., F.R.S.
Physical, 5.
- SATURDAY, 23rd.**—Royal Institution, 3. "The Artificial Production of Cold," by H. Graham Harris, M.Inst.C.E.

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AND

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THE CHEMICAL NEWS.

VOL. LXIII., No. 1643.

THE VOLUMETRIC COMPOSITION OF WATER.

By EDWARD W. MORLEY.

(Concluded from p. 232).

Determination of Nitrogen contained in the Hydrogen used for Determination of the Volumetric Composition of Water.—The parts p , q , r , were exhausted, filled with hydrogen, from n , and again exhausted. The pressure of the gas in n was then measured by means of m , and its temperature by thermometers at n . From this, with the known volume of n , and its connections, could be computed the reduced volume of the gas in n ; then r was heated, and the valve o was opened. When about a litre of hydrogen had been taken from n , o was shut, and the volume remaining was determined. The heating of r was continued till the gas remaining was reduced to some such volume as ten cubic centimetres, when r was cooled, and the gas was extracted by the Sprengel pump. A suitable excess of oxygen was extracted from its store, the two gases were measured, mixed, exploded, and the residue measured. From this was computed the amount of hydrogen found by analysis, whence was learned by difference the amount of nitrogen which was originally contained in the volume known to have been extracted from n .

To illustrate by an actual experiment: In n , before extracting any hydrogen, the temperature and pressure were 766.5 m.m., 20.5 degrees; after, 662.0 m.m. and 20.9 degrees. Hence it was computed that 823 c.c. had been admitted to r . When r was cold, the hydrogen remaining was extracted, and transferred to the apparatus shown in Fig. 3, and found to be 6.722 c.c. at standard temperature and pressure. Oxygen was added, and the sum found to be 17.101 c.c. After explosion there remained 7.019 c.c. Hence the hydrogen found in the 6.722 c.c. taken for analysis was 6.721 c.c. A duplicate analysis agreed well with this; so that this hydrogen was practically free from nitrogen.

Determination of the Volumetric Composition of Water.—Two jars of hydrogen were extracted from n without heating r , and a jar of oxygen from the store of oxygen. I measured a convenient volume of hydrogen; for ease of explanation, suppose it was 180 c.c. About 120 c.c. were transferred after measurement to a jar in the cistern, and the other 60 to a second jar. Then a volume of oxygen either a little smaller or a little larger was measured; suppose it was 175 c.c. After measurement, it was transferred to three jars, 60 c.c. to the jar having 120 of hydrogen, 60 to the other jar of hydrogen, and 55 to a small graduated jar. Another volume of hydrogen was next measured, say 179 c.c. One-third of this was put into the jar into which the smaller quantity of hydrogen had been put before, and the remaining 120 c.c. were left in the eudiometer.

It will be noticed that the three measurements are made at as nearly the same point as is consistent with the fact that there must be a slight excess of either one gas or the other. It would probably have been better to have made the three volumes as nearly equal as possible, and then to have measured a small excess at the point at which the excess was to be measured after the explosion. But this was not thought of in time. As it was, errors of calibration could have no great effect; but they were further made of still less effect on the final mean in two ways. In some experiments, the hydrogen was put in excess, and in some, oxygen; if in two such experiments

the sum of the two gases were the same, the points of measurement of oxygen and of hydrogen would be interchanged, and the errors of calibration would produce contrary effects. Again, the amounts of gas taken were increased from time to time, so that all points from 63 to 75 centimetres were used, by which also accidental errors in calibration were rendered of small influence on the result.

The measured gases were now ready for explosions in fractions. Explosions were always made in the presence of a large volume of inert gas. The ratio of explosive gas to inert was varied within somewhat wide limits, and the same ratio was preserved throughout all the explosions of a given experiment. Suppose that in a given case the ratio desired was that of four to one. To the 120 c.c. of hydrogen left in the eudiometer were added 30 from one of the jars containing hydrogen and oxygen. After this was exploded, a like volume was added again, and so on, till all the gas previously mixed had been consumed. There would still be 120 c.c. of hydrogen in the eudiometer. To this was now added eight c.c. of oxygen from the small graduated jar. The two were mixed by letting mercury drop through the eudiometer, and were exploded. A smaller computed volume of oxygen was added and mixed for the next explosion, and so on, till all the oxygen was finally exploded in presence of fifteen times its volume of hydrogen. But when oxygen was to be finally in excess, a variation was made a little before the last explosion, by adding small quantities of hydrogen to an excess of oxygen in the eudiometer; up to this point, hydrogen was kept in excess. It is obvious that the last explosion of the series is the critical one on whose completeness accuracy depends; sufficient attention was given to this matter.

After the explosion was completed, it cost some trouble to put the eudiometer into condition for good measurement, because so much water had accumulated in it. Then an excess of oxygen or of hydrogen, as the case might be, was added, the mixture was exploded, and the residue was measured. From this was computed the amount of nitrogen in both gases taken together; subtracting the nitrogen known to exist in the hydrogen according to the previous experiment, the remainder was the nitrogen in the oxygen used. The ratio of the volumes of hydrogen to oxygen in water could then be computed. As to the chemistry, consumption of oxygen by oxidation of mercury or of fat, and the possible production of hydrogen dioxide, had to be considered.

When mercury is oxidised in the eudiometer, it is by the oxidation of fine globules on the walls of the eudiometer. In mixing the last third of the oxygen with hydrogen, it was convenient to let a current of mercury run down through the eudiometer, which covered its walls with mercury. In three experiments, some of this mercury was oxidised; two experiments were lost. In the other, it was found possible to reduce the oxidised mercury by a managed explosion, so that the water produced was perfectly clear, as it was in all the other experiments.

There was no carbon in my gases before they were measured. In two experiments, when the eudiometer had not been cleaned, carbon dioxide was produced. This must have come from fat on the walls of the eudiometer forced down by the current of mercury which mixed the oxygen and hydrogen. Since the composition of the lubricant was well enough known, it was possible to add to the oxygen used in producing carbon dioxide the amount used in the combustion of the hydrogen of the fat, and so deduce the value of the ratio sought. As to hydrogen dioxide, in the absence of sufficient knowledge of what might take place in an excess of oxygen, hydrogen was kept in excess till nearly the end of the series of explosions.

To illustrate by an actual experiment, I will give all details of experiment number 6. The first column gives the temperatures, the second the readings of the scale of

the endiometer, the third gives the reduced volume of gas deduced from each measurement, and the fourth gives the adopted mean, with the name of the gas measured.

Temperature.	Pressure.	Volume reduced.	Means.
19°87	688°75	174°333	174°33 hydrogen.
19°89	688°76	174°326	
20°26	680°62	169°954	
20°29	680°65	169°947	169°95 oxygen.
19°44	685°45	172°910	
19°47	685°47	172°905	
19°59	679°98	172°920	172°91 hydrogen.
20°18	137°92	7°797	
20°54	138°08	7°805	
20°73	255°54	25°271	7°80 residue.
21°78	256°02	25°269	
21°80	187°06	13°829	
21°76	187°05	13°830	25°27 residue and oxygen.
			13°83 residue 2.

1. $\frac{1}{2}(25°27 - 13°83) = 7°62$ c.c., hydrogen in residue 1.
2. $7°80$ c. - $7°62$ c. = $0°18$ c.c., nitrogen in residue 1.
3. $0°18$ c.c. - $0°00$ = $0°18$ c.c., nitrogen in oxygen used.
4. $\frac{174°33 + 172°91 - 7°62}{169°95 - 0°18} = 2°00047$; ratio sought.

The experiments made divide themselves into groups according to the purity of the gases used. In some, both gases contained nitrogen, in some only the hydrogen, in some only the oxygen, and in some both gases were pure; in some carbon dioxide was produced, although both gases were pure. I give in full the quantities measured or the quantities computed from them in the case of the first experiment of each of these groups; but I selected the eighteenth experiment, rather than the

seventeenth, so as to include one in which there was an excess of oxygen.

In the accompanying table I give the approximate temperature and pressure at which the hydrogen and oxygen were measured in each experiment, the amounts of impurities found in each gas, and the amounts of hydrogen and oxygen consumed in the explosion, with the ratio thence deduced. The pairs of determinations which are bracketed together were made one immediately after the other of the pair, with the same stores of gas extracted at the same time, and as nearly as possible under the same conditions, except that different gases were in excess. This will explain why the amounts of impurities found in the oxygen used should show such agreement. The oxygen used in the experiments from the fourth to the twelfth was obviously undergoing slow admixture with air, which was suffered to continue in order to see if the presence of nitrogen affected the ratio found. After a while, the crack in a glass tube which had shown itself was closed by fusion.

Comparison of Results.

Experiment 1 is alone in showing impurity in both gases; its result gives $2°00027$ for the value sought.

Experiments 2 and 3 showed nitrogen in the hydrogen; their mean is $2°00029$.

Experiments from 4 to 12 showed nitrogen in the oxygen; their mean is $2°00021$.

Experiments 13 to 17 and experiment 20 showed no measurable impurity in either gas; their mean is $2°00023$.

In experiments 18 and 19 carbon dioxide was produced; their mean is $2°00025$.

The mean of the seven experiments where oxygen is in excess is $2°00023$, and that of the thirteen in which

Number.	Pressure.	Temperature.	Hydrogen taken.	Oxygen taken.	Residue.	Hydrogen in residue.	Oxygen in residue.	Nitrogen in hydrogen.	Nitrogen in oxygen.	Carbon dioxide formed.	Oxygen consumed.	Amount to be subtracted from hydrogen.	Amount to be subtracted from oxygen.	Hydrogen used.	Oxygen used.	Ratio.
C.m.	°	C.c.	C.c.	C.c.	C.c.	C.c.	C.c.	C.c.	C.c.			C.c.	C.c.			
1	64	22	307°89	150°03	8°29	8°015	—	0°11	0°165	—	—	8°12	0°165	299°77	149°865	2°00027
2	64	22	307°29	149°28	8°68	8°57	—	0°11	0°00	—	—	8°68	0°00	298°61	149°28	2°00033
4	66	20	325°36	156°21	13°36	13°21	—	0°00	0°15	—	—	13°21	0°15	312°15	156°06	2°00019
14	72	23	383°30	185°70	11°87	11°87	—	0°00	0°00	—	—	11°87	0°00	371°43	185°70	2°00016
18	75	25	407°98	205°71	1°73	—	1°66	—	—	0°065	0°09	0°00	1°75	407°98	203°96	2°00029

Number.	Temperature.	Pressure.	Nitrogen in hydrogen.	Nitrogen in oxygen.	Carbon diox. produced.	Oxygen consumed.	Hydrogen consumed.	Oxygen consumed.	Ratio.	Gas in excess.
	°									
1.	22	64	0°11	0°165	—	—	299°77	149°865	2°00027	Hydrogen.
2.	22	64	0°11	0°00	—	—	298°61	149°28	2°00033	Hydrogen.
3.	19	66	0°12	0°00	—	—	316°45	158°205	2°00025	Hydrogen.
4.	20	66	0°00	0°15	—	—	312°15	156°06	2°00019	Hydrogen.
5.	20	66	0°00	0°15	—	—	325°36	162°67	2°00012	Oxygen.
6.	20	70	0°00	0°18	—	—	339°62	169°77	2°00047	Hydrogen.
7.	20	70	0°00	0°18	—	—	347°24	173°60	2°00024	Oxygen.
8.	20	72	0°00	0°31	—	—	364°58	182°28	2°00011	Hydrogen.
9.	20	72	0°00	0°31	—	—	386°65	193°31	2°00016	Oxygen.
10.	22	72	0°00	0°72	—	—	381°85	190°92	2°00005	Hydrogen.
11.	22	72	0°00	0°82	—	—	389°79	194°87	2°00026	Oxygen.
12.	22	73	0°00	0°82	—	—	395°75	197°85	2°00027	Hydrogen.
13.	23	71	0°00	—	—	—	372°09	186°01	2°00038	Hydrogen.
14.	23	72	0°00	0°00	—	—	371°43	185°70	2°00016	Hydrogen.
15.	23	72	0°00	0°00	—	—	383°30	191°62	2°00031	Oxygen.
16.	26	73	0°00	0°00	—	—	383°51	191°74	2°00016	Hydrogen.
17.	26	73	0°00	0°00	—	—	392°58	196°27	2°00021	Oxygen.
18.	25	75	0°00	0°00	0°065	0°09	399°74	199°85	2°00020	Hydrogen.
19.	25	75	0°00	0°00	0°065	0°09	407°98	203°96	2°00029	Oxygen.
20.	24	75	0°00	0°00	—	—	399°21	199°59	2°00015	Hydrogen.

hydrogen was in excess is also 2'00023. Weights were originally assigned to each result according to the circumstances of each experiment, but they did not change the final mean, and are not given. Four experiments were lost by accident, all others are given. The mean error of a single determination of the ratio is 0'000075, or one part in 26,000. The final mean value of the ratio is 2'0002.

Summary.

Pure hydrogen cannot be obtained from the purest commercial zinc. By the electrolysis of dilute sulphuric acid, with a proper purifying train, I have obtained hydrogen containing less than the hundredth of a c.c. of nitrogen in two litres of hydrogen, and containing no other impurity in amount large enough to be detected. By the use of a fusible metal valve it was possible to obtain any required degree of exhaustion in the part of the apparatus designed to receive hydrogen from the generator. The hydrogen intended to be weighed was not suffered to take up mercurial vapour, nor that intended for analysis to be contaminated with organic matter. A supply of hydrogen sufficient for several experiments was so stored up as to be safe from admixture of air, so that by the apparatus described the amount of nitrogen in it could be determined in duplicate, and other quantities identical in composition could be used for determining simultaneously the amount of nitrogen in the oxygen used, and also the volumetric composition of water. An apparatus for the measurement of gases has been constructed in which the mean error of measurement of the volume of hydrogen and oxygen used in the experiments has been less than one part in fifty thousand. With this, twenty experiments have been made (four others being lost by accident and not completed), which gave a maximum value for the composition of water 2'00047, a minimum value 2'00005, and a mean value 2'00023. Variations in the process gave no corresponding variation in the result. The mean error of a single determination was one part in 26,000.

For the present, then, we may believe that water, when the gases are measured under ordinary temperatures and pressures, is composed of 2'0002 volumes of hydrogen to one volume of oxygen; or that under ordinary conditions the number of molecules in a given volume of oxygen is 1'00002 part greater than the number of molecules in an equal volume of hydrogen.

SILICON FILIMS.

By H. N. WARREN, Research Analyst.

In the CHEMICAL NEWS (vol. lviii., p. 215), I published a short account of the production of silicon hydride, noting its peculiar properties; since that period recent investigations upon this and other gases have led to valuable results. Before stating the decomposition of this substance into its component parts, I will give a brief outline of the induction coil employed which was of special construction, the core, or magnet, consisting of two pounds of chemically pure iron wire, upon which was wound about a pound of very thick copper wire, the whole being enclosed in a thick ebonite tube and filled up with pure paraffin wax. This, on being connected to a condenser of 280 sheets of tin-foil, constitutes the primary coil; over this tube was wound in 25 segments, each one being insulated from the other by means of mica disks, 92 lbs. of No. 26 copper wire of double silk covering, the object of using so thick a grade being to increase the width of the spark in proportion to its length; the whole was now coated with paraffin, covered with thick vulcanite, and mounted. By the aid of six Bunsen batteries, a spark of six inches in length and of considerable width was thus obtained, the intensity being sufficient to pierce oak planks one quarter of an inch in thickness.

To prepare the silicon hydride, magnesium silicide was

obtained by passing over metallic magnesium heated to dull redness a slow stream of silicon fluoride, until half the metal was consumed. The mass was now withdrawn from the tube and melted under a flux composed of a mixture of magnesium, potassium, and sodium chloride, a button of magnesium silicide being thus produced. This was at once introduced into an apparatus for evolving hydrogen gas, and connected to a glass tube through which passed the two electrodes in connection with the induction coil, the apparatus being cleared of the atmospheric air it contained by acting upon metallic magnesium contained therein previous to the introduction of the silicide. When the whole of the atmosphere was thus abstracted, the silicon hydride was evolved by the addition of acetic acid; the current from the coil was now turned on, amorphous silicon being at once deposited upon various parts of the glass tube, but not until the two points were in close proximity to each other did any appearance of a compact film begin to manifest itself. This, when once started, increased in length upon the withdrawal of the electrodes to a more remote distance, filling up the luminous arc and spreading out towards the further electrode; the silicon thus produced was undoubtedly absolutely pure, and when exposed to the flame of a Bunsen burner became converted into a white ash consisting of pure silica.

The gas, in admixture with coal gas, was next treated, and was readily decomposed, yielding a film consisting of a mixture of silicon and carbon. The idea of utilising these so produced films for electro-incandescent lamps was naturally one of the first prospects which presented itself; but on account of the silicon appearing mostly as amorphous, it is not sufficient to protect a carbon film over a certain time. It has nevertheless been the means, however, of carrying out an entirely different, and at the same time efficient and simple process, whereby a dense silicon of peculiar formation has been so produced that several carbon films that have been thus coated have even withstood the action of the atmosphere for long durations.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

ANALYSIS OF A CHROMITE.*

By H. PEMBERTON, jun.

On the Pacific Coast of the United States there are several deposits of chromite. As no complete analysis of any of these minerals has, to my knowledge, been published, it may be of interest to place on record an analysis I made some time ago.

According to Wm. Ireland, jun., State Mineralogist of California, throughout the Santa Lucia Mountains and the coast hills of San Luis, Obispo County, Cal., are found serpentine rocks with beds of chromite, in greater or less masses, existing as loose and fragmentary rocks in the ravines and on the hillsides, and as pockets and veins on the mountains. One of the best mines of the neighbourhood is the Pick and Shovel, located on the South Fork of Chorro Creek, at an elevation of 1800 feet.

A sample of the chromite from this mine, selected as free from gangue as possible, gave an analysis in the following results:—

Cr ₂ O ₃	..	..	..	52'68
Al ₂ O ₃	..	..	..	11'40
Fe ₂ O ₃	..	..	..	3'52
MgO	..	..	..	16'23
FeO	..	..	..	11'77
MnO	..	..	..	0'15
SiO ₂	..	..	..	3'40
H ₂ O	..	..	..	0'94

100'09

* Read at the Chemical Section of the Franklin Institute, March 17, 1891.

An analysis of the gangue showed it to be serpentine, containing a trace only of ferrous oxide. No other foreign mineral could be detected on a careful examination. Deducting, therefore, the water, silica, and quantity of magnesia (3.26 per cent) combined with the silica (as serpentine) and calculating the remainder to 100 parts, we obtain for the pure mineral:—

Cr ₂ O ₃		56.96	0.374	
Al ₂ O ₃		12.32	0.121	} = 0.519
Fe ₂ O ₃		3.81	0.024	
MgO..		14.02	0.350	
FeO ..		12.73	0.177	} = 0.529
MnO..		0.16	0.002	
		100.00		

$$R_2O_3 : RO = 519 : 529 = 1.00 : 1.02.$$

The mineral was decomposed by fusion with sodium carbonate. (Christomanos' process slightly modified). The mixture of ore and Na₂CO₃ is heated over night by a Bunsen burner, the crucible being loosely covered by its lid. Next morning it is heated for one hour over the blast lamp, with frequent stirring. The process has the advantage of giving complete decomposition of the mineral, with the introduction of no bases other than the alkalis.

The ferrous oxide was determined by solution in sulphuric acid in a closed tube, under pressure. According to Francis C. Phillips (*Fres. Zeitschrift*, xii., 189), 1.34 is the specific gravity of the acid that is most favourable to the solution of chromite in this manner.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

May 7th, 1891.

Dr. J. H. GLADSTONE, F.R.S., Vice-President, in the chair.

CERTIFICATES were read for the first time in favour of Messrs. Edward Brown, 32, Courlandsky Street, St. Petersburg; Ernest A. Congdon, Lehigh University, St. Bethlehem, U.S.; W. Porter Draper, 1, Ceal Villas, Ceal Road, Enfield; Thomas Mitchell, c/o E. Mitchell, Crossmount, Bridgend, N.B.; H. J. Marston Mousley, Kingsbury, Portland Road, Edgbaston; Edward Rhodes, Holybank, Frodsham, Cheshire; John Taylor, 15, Lucius Street, Torquay.

The following were elected Fellows of the Society:—Messrs. Edward Arthur Barnes, William Bate, Claude Hooper Bate, Albert Edward Bell, Rhys Pendrill Charles, Walter Johnson Cooper, Frederick Arthur Evans, Gilbert John Fowler, Joseph Fitze, John Alfred Foster, Berington H. Gibbins, William L. Hiepe, Ph.D., William Beaumont Hart, Walter Herbert Joseland, F. Stanley Kipping, D.Sc., Alexander Lauder, Rev. Edgar Norman Langham, James Leicester, George R. Morrison, William Macdonald, Charles Ainsworth Mitchell, Frederick Johnson Merrills, Lewis Ough, Percy Morris Randall, James Ashburner Storey, Albert Searl, James Fowler Tocher, Cecil George Freer Thonger, M.R.A.C., John Wild.

The Chairman announced that since the last meeting of the Society took place a congratulatory address, of which the following is the text, had been forwarded to Professor Stas:—

We, the President, Officers, and Council, on behalf of the Chemical Society, most heartily congratulate you, Professor Jean Servais Stas, on the completion of your fiftieth year of membership of the Royal Belgian Academy of Sciences, Literature, and Arts.

Among the names of the distinguished investigators who have raised chemistry to the dignity of an Exact Science, none either merits or receives a more honoured position than that of Stas. Your researches are universally recognised among men of science as of fundamental importance. By your incomparable determinations of the atomic weights of a large number of the more important elements you have not only placed in our hands numerical data of the utmost value, but your researches are models which must ever serve to show how such determinations should be effected and the innumerable precautions which must be taken. Concerning these precautions comparatively few, even among chemists, fully realise the extent to which they have been shown by you to be necessary: those who have been engaged in similar investigations can only entertain an admiration almost reverential in character for the man who could plan and successfully carry out a prolonged series of such refined, tedious, and delicate operations. A most important result of your inquiries has been the refutation, in its original form at least, of the famous hypothesis of Prout: your marvellously accurate determinations showing that it is no longer possible to believe that the atomic weights of the elements are expressible as a series of multiple whole numbers. With strict logical propriety you have refrained from pronouncing any opinion in explanation of the discrepancy; the data which you have established, however, will surely serve in the future as the groundwork of further discussion of the problem of the mass relationship of the elements. The methods which you have devised for the preparation of pure substances have, in many cases, in themselves been important contributions to chemical science; and the service which you have rendered by teaching the chemist how to prepare pure reagents is of the utmost value. Hence your *Recherches sur les Rapports réciproques des Poids atomiques* must be handed down to future generations as one of the most valuable classics of the Exact Sciences. Apart from the intrinsic value of your work, you have through it exercised a beneficent influence on your colleagues throughout the world, the importance of which cannot be over-estimated; and in the eyes of chemists generally, you are ever regarded as an honour to Science, to your country and to the distinguished Academy of which you have now been an ornament for half a century.

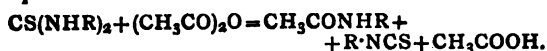
The following papers were read:—

II. *The Action of Alkalis on the Nitro Compounds of the Paraffin Series.* By WYNDHAM R. DUNSTAN and T. S. DYMOND.

The authors have further investigated the conditions and products of the interaction of alkalis and nitroethane, of which they have already given a preliminary account to the Society (*Proc.*, 1888, 117).

Nitroethane attacks alkali carbonates in the cold with formation of carbon dioxide and the alkali derivative of nitroethane which is also obtained when alkali hydroxide is employed. Ammonia combines with nitroethane in the cold to form a crystalline compound analogous to the potassium and sodium derivatives. The action of alkalis does not appear to proceed further at atmospheric temperatures, but on warming, alkali nitrite, acetonitrile, and a new compound, boiling at 170° and freezing to a crystalline solid at 3.5°, are produced. The new compound is a feeble base, which forms unstable salts decomposed by water: the *mercurichloride* has the formula C₆H₉NO.HgCl₂, and the *aurichloride* the formula C₆H₉NO.AuCl₃. It is remarkable for its great stability, being almost unaffected by heating in closed tubes with strong acids and alkalis. Permanganate oxidises it to acetic acid, and nitric acid to acetic and oxalic acids. It is hard to attack with the usual reducing agents, but is slowly decomposed with formation of ammonia, acetic acid, and secondary butyl alcohol. By acting with sodium on a well cooled moist ethereal solution, a

into "anilid" and mustard oil in accordance with the equation—



3. Five minutes heating at the boiling point of acetic anhydride gives an almost theoretical yield of mustard oil.

4. An extension of the time of heating induces a secondary interaction between the mustard oil and acetic acid, whereby the yield of the former is rapidly diminished, viz.:—



Curves are given in the original paper, showing the influence of time on the rate of fall in the yield of mustard oil.

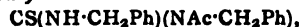
In the case of the paraffinoid thiocarbamides the results are different.

1. A well defined acetylated thiocarbamide is first produced.

2. Further heating gives rise to the formation of mustard oil, but the yield of the latter is never high, on account of the secondary interaction proceeding simultaneously with the generation of the mustard oil.

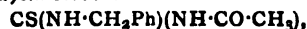
3. Prolonged heating gives a substituted amide as final product.

Acetyldibenzylthiocarbamide—



prepared from dibenzylthiocarbamide, crystallises from alcohol in prisms; m. p. 93°C . The alcoholic solution is not desulphurised by boiling with alkaline lead tartrate. With $\text{AgNO}_3\cdot 2\text{NH}_3$ it gives a white precipitate. It decomposes partly on distillation, yielding between 175 — 180° an oil rich in sulphur, and between 180 — 190° the distillate solidifies to a substance which after purification forms colourless crystals melting at 60 — 61° and free from sulphur.

Acetylbenzylthiocarbamide—



was incidentally prepared from acetic anhydride and monobenzylthiocarbamide. It crystallises from alcohol in thin rhombic prisms; m. p. 129 — 130° . The alcoholic solution, unlike that of the previous compound, desulphurises alkaline lead solution on boiling, and with $\text{AgNO}_3\cdot 2\text{NH}_3$ gives a white precipitate which darkens on standing, and is immediately blackened on boiling. On distillation, the urea decomposes partly into CH_3CONCS and benzylamine and partly into benzylthiocarbamide and acetamide.

14. "The Decomposition of Silver Chloride by Light." By ARTHUR RICHARDSON, University College, Bristol.

The author describes experiments which have been made with a view to determine whether silver chloride which has been darkened by exposure to light under water contains oxygen. The nature of the change which occurs during decomposition of the chloride was also studied with reference to the part played by water.

Pure silver chloride was prepared by addition of dilute chlorhydric acid to a solution of pure silver nitrate, the precipitate being washed by decantation till free from acid. The following facts were observed during exposure:—

(1.) Oxygen was evolved, a part of which was present as ozone.

(2.) When small quantities of water were present, chlorine and hydrogen chloride were found in solution.

(3.) When a large volume of water was taken, hydrogen chloride but no chlorine was detected.

The influence of hydrogen chloride in retarding the decomposition of silver chloride is considered, and is explained from experimental results given, which show that even minute quantities of hydrogen chloride exercise a marked influence on the stability of chlorine water when exposed to light, the rate of decomposition of the silver

chloride being dependent on the readiness with which the chlorine in solution and water interact to form hydrogen chloride. Thus, when silver chloride was exposed to light in a solution of hydrogen chloride containing 0.9 part per 100 of solution, the total chlorine liberated was 0.201 gm., of which 13.7 per cent represented free chlorine, whilst for the same weight of silver salt in pure water the total chlorine found was 0.276 gm., of which 0.9 per cent was present as free chlorine.

In the examination of the darkened product for oxygen, a portion of the substance was taken which had lost 8 per cent of its total chlorine during exposure. After it had been dried at 110°C . till it ceased to lose weight, it was heated in a current of pure hydrogen, the gaseous products of the reduction being passed through a weighed phosphorus pentoxide tube. Before using this substance as an absorbent of moisture, it was ascertained that hydrogen chloride was not absorbed by it after contact for a few hours only, as the weight of the tubes remained unaltered in contact with the dry gas. The hydrogen was prepared by the action of steam on sodium, numerous precautions, which are described in full in the paper, being taken to preclude errors.

The results show that the gain in weight of the drying tubes after the decomposition of the silver compound, which lasted from 7—8 hours, is so small as to preclude the possibility of the presence of an oxygen compound in the darkened product. The darkening of the carefully dried chloride was also observed to take place when exposed to light in a tube containing dry carbon tetrachloride from which all air had been removed by boiling. From these facts the author concludes that the darkened silver compound is of the nature of a subchloride rather than an oxychloride.

15. "The Addition of the Elements of Alcohol to the Etheral Salts of Unsaturated Acids." By T. PURDIE, Ph.D., B.Sc., and W. MARSHALL, B.Sc.

In this paper the authors record the results of further experiments on the addition of the elements of alcohol to etheral salts of fumaric and maleic acids by the agency of small quantities of sodium alkylate; they also describe a series of similar experiments with other etheral salts, the object of which was to ascertain if the etheral salts of unsaturated acids in general are capable of undergoing the same additive change.

By the action of small quantities of sodium methylate in the cold on a mixture of methyl alcohol and methylic fumarate, the latter is converted, almost quantitatively, into methylic methoxysuccinate, which crystallises in very large and perfectly developed crystals melting at 28° . Methylic methoxysuccinate from methylic maleate is identical with that obtained from methylic fumarate. Methoxysuccinamide, from the action of alcoholic ammonia on the etheral salts, melts at 175° .

From the product of the action of alcoholic sodium methylate on methyl fumarate aided by heat, an amorphous substance was obtained, the composition of which agreed with that of a compound having the formula $\text{C}_{11}\text{H}_{12}\text{O}_7$, formed by the abstraction of 3 mols. of methyl alcohol from 2 mols. of methylic methoxysuccinate.

By the action of small quantities of sodium methylate on a mixture of methylic acrylate and methyl alcohol, methylic methoxypropionate was obtained.

Methylic and ethylic crotonate gave, in a similar manner, methylic methoxybutyrate and ethylic ethoxybutyrate respectively. The metallic salts of these acids are mostly gums or resins, but the acid amines are crystalline; the methoxybutyramide melts at 69° , and the corresponding ethoxy-derivative at 75° . The authors think that in the interaction under consideration, the alkoxy-group attaches itself to the β -carbon atom, but the evidence on this point is not conclusive.

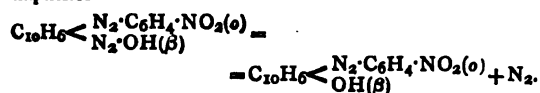
Ethylic methacrylate seems also to be capable of combining with the elements of alcohol, but pure products were not obtained.

Ethylc angelate, ethylc allylacetate, methylc and ethylc cinnamate, and ethylc α -(β -ethylcumarate were found incapable of the additive change under investigation. Similar experiments were made with ethylc phenylpropionate, but no additive product was obtained.

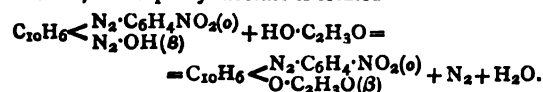
The ethereal salts of unsaturated acids differ greatly in respect of their capability of combining with the elements of alcohol under the agency of sodium alkylate. This capability is, no doubt, affected by the position of the doubly-linked carbon atoms and by the nature of the atomic groups with which they are united. It is, however, impossible at present to draw any general conclusion regarding the influence of these factors.

16. "Notes on the Azo-derivatives of β -naphthylamine." By RAPHAEL MELDOLA, F.R.S., and FRANK HUGHES.

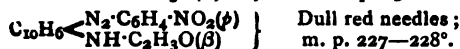
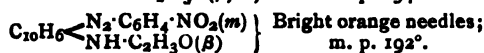
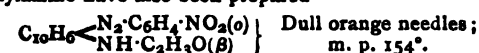
The authors have completed the series of azo-derivatives obtainable from the nitranilines and β -naphthylamine by preparing orthonitrobenzeneazo- β -naphthylamine. This compound crystallises in bronzy scales; m. p. 198°. When acted on by sodium nitrite in a warm glacial acetic acid solution, it gives orthonitrobenzeneazo- β -naphthol—



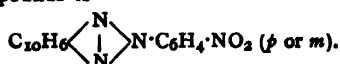
The latter forms bright red needles; m. m. 209—210°. When the interaction is effected in a cold acetic acid solution, the naphthyl acetate is formed—



The latter is a deep red oil, from which the acetyl group is easily removed by alkalis. Acetyl derivatives of the ortho-, meta-, and para-nitroso-derivatives of β -naphthylamine have also been prepared—



The pseudazimides from the para- and meta-nitro-compounds have been prepared by Zincke's method of oxidation with chromic acid in glacial acetic acid solution. The first of these crystallises in flat, colourless needles, m. p. 236°, and the second in whitish needles of m. p. 224°. The ortho-compound gives but a very small quantity of pseudazimide on oxidation. The formula of these compounds is—



The action of aldehyds on these β -naphthylamine azo-derivatives gives rise to the formation of triazines, which are being investigated. Fuming nitric acid in the cold converts the azo-compounds into orange, amorphous products which are apparently definite but difficult to purify and explosive.

17. "The Estimation of Nitrates." By G. McGOWAN, Ph.D.

The author describes a method of estimating nitrates based on the interaction



The nitrate is warmed together with an excess of concentrated chlorhydric acid in an apparatus from which air has been expelled by CO_2 , and the gaseous products are led into a solution of potassium iodide; an amount of iodine is liberated equivalent to the whole of the chlorine carried forward, nitric oxide escaping, i.e., $\text{HNO}_3 = 3\text{Cl}$.

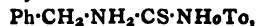
18. "New Benzylc Derivatives of Thiocarbamide." By AUGUSTUS E. DIXON, M.D.

A re-examination of "monobenzylthiocarbamide" has shown that the substance hitherto bearing this name is really benzylamine thiocyanate; the latter can be converted into the isomeric thiocarbamide by heating for a short time at 150—160°. The melting-point recorded for symmetrical dibenzylthiocarbamide also requires correction; it lies between 146° and 147°, and not at 114°, as stated.

The following compounds are described:—

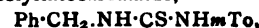
Benzylthiocarbamide, $\text{Ph} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_2$, small white prisms; m. p. 161—162°.

Benzylorthotolylthiocarbamide—



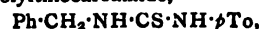
white, rhombic prisms; m. p. 138—139°.

Benzylmetatolylthiocarbamide,—



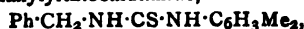
glassy clear rhombs, m. p. 113—114°.

Benzylparatolylthiocarbamide,—



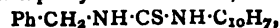
glassy rhombic crystals; m. p. 120—121°.

Benzylmetaxylthiocarbamide,—



large colourless monoclinic prisms; m. p. 84—85°.

Benzylalphanaphthylthiocarbamide,—

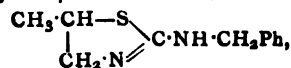


micaceous-looking rhombs; m. p. 172—173°.

Benzylbetanaphthylthiocarbamide rhombic plates; m. p. 165—166°.

Allylbenzylthiocarbamide, $\text{Ph} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{All}$, colourless rhombic crystals; m. p. 93—94°. Converted by heating with HCl at 100° into—

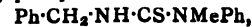
Benzylpropylene- ψ -thiocarbamide,—



fine white needles; m. p. 65—66°.

Acetylbenzylthiocarbamide, $\text{Ph} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CS} \cdot \text{NHAc}$, thin pearly plates; m. p. 128—129°.

Benzylmethylphenylthiocarbamide,—



white prisms; m. p. 84—85°.

Methylphenylbenzylthiocarbamide,—



shining white prisms; m. p. 120—121°.

Benzylethylphenylthiocarbamide,—



long slender oblique prisms; m. p. 90—91°.

Ethylbenzylphenylthiocarbamide,—



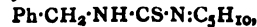
short thick rectangular prisms; m. p. 90.5—91°.

Benzylphenylbenzylthiocarbamide,—



white pointed prisms; m. p. 102—103°.

Benzylpiperidylthiocarbamide,—



waxy-looking prisms; m. p. 85—88°.

19. "Interaction of Phenylthiocarbimide and Acetic Acid." By EMIL A. WERNER, Trinity College, Dublin.

This interaction was originally made the subject of an experiment by Professor von Hofmann, and later on by Claus and Völtzkow; the former considered diacetanilid to be the product, while the latter simply mention acetanilid as being formed.

In neither case was the examination of the products exhaustive. The author has made a careful re-investigation of the subject, and wishes to state his results at once, as an abstract of a paper, by Messrs. Cain and Cohen, on

the same interaction, appeared in the last *Proceedings*. The author agrees with Messrs. Cain and Cohen, that diacetanilid is not formed, but his results oblige him to differ entirely from these gentlemen with respect to the course of the change.

The influence of water on the nature of the interaction is very marked. With *pure anhydrous* acetic acid and phenylthiocarbimide, interaction takes place, *quantitatively*, at 130–140°, in accordance with the equation: $C_6H_5NCS + CH_3COOH = CH_3CONHC_6H_5 + COS$.

If the acid *contain water*, H_2S , CO_2 , and diphenylurea are formed as products of a secondary change, viz., $2C_6H_5NCS + 3H_2O = CO(NHC_6H_5)_2 + CO_2 + 2H_2S$.

At a higher temperature, 160–170°, the diphenylurea disappears, through interaction with acetic acid, thus: $CO(NHC_6H_5)_2 + 2CH_3COOH =$



the extent to which this change takes place increases, within certain limits, with the proportion of water present in the acid.

Propionic acid and phenylthiocarbimide interact in a similar manner, but with formic acid a secondary interaction takes place, which appears to be independent of the presence of water.

Research Fund.

Fellows desiring grants are requested to forward their applications to the Secretaries, in order that they may be considered at a meeting early in June.

PHYSICAL SOCIETY.

April 17th, 1891.

VISIT OF THE PHYSICAL SOCIETY OF LONDON TO CAMBRIDGE.

ON Saturday, the 9th inst., the Society varied its ordinary procedure by paying a visit to the ancient seat of learning situated on the banks of the Cam.

Assembling at Liverpool Street Station, members and visitors to the number of about one hundred were conveyed in saloon carriages by the 11 o'clock express direct to their destination, the whole journey being accomplished in about seventy-five minutes.

Amongst those present were Dr. E. Atkinson, Prof. Ayrton and Mrs. Ayrton, Mr. Walter Bailey, Mr. Shelford Bidwell and Mrs. Bidwell, Mr. D. T. Blaikley, Mr. T. H. Blakesley and Mrs. Blakesley, Mr. J. T. Bottomley, Mr. C. V. Boys, Prof. Carey Foster, Mr. Conrad W. Cooke, Prof. Fitzgerald, Dr. E. Frankland and Mrs. Frankland, Dr. W. R. Hodgkinson, Prof. O. J. Lodge, Prof. Meldola, Prof. Perry and Mrs. Perry, Prof. Rücker, Dr. Sumpner, Prof. S. P. Thompson and Mrs. Thompson, Mr. A. P. Trotter and Mrs. Trotter, and Mr. G. M. Whipple.

On arriving at the historic town the party became the guests of the Cambridge members, and proceeded to Emmanuel College, where they were received by Mr. W. N. Shaw, M.A. Various groups visited "The Cloisters," chapel, and gardens, and at 1 o'clock lunch was provided in the College Hall.

At 2.30 a meeting of the Society was held in the Lecture Room of the Cavendish Laboratory. The papers read were all by authors resident in Cambridge, and the abstracts given below will sufficiently indicate the variety of the subjects brought before the Society. After the meeting, the visitors inspected the Cavendish Laboratory. Amongst the many interesting instruments and apparatus to be seen, specially noticeable were Prof. J. J. Thomson's 50 feet vacuum tube glowing from end to end with a luminous discharge; Mr. Shaw's pneumatic bridge, by which the pneumatic resistance or conductivity of various shaped orifices and channels can be compared; and the new air condensers to be used by Mr. Glazebrook as standards.

The Cambridge Scientific Instrument Company had an interesting exhibit, including a dividing engine, Boys' radio-micrometer, electrically-driven tuning-forks, and various recording instruments, amongst which was Galton's apparatus for registering the growth of plants.

Other things which attracted attention were Glazebrook's spectrophotometer; Lord Rayleigh's coils and apparatus used in his determination of the ohm; a collection of models, medals, and instruments formerly belonging to Professor Maxwell; the resistance standards of the British Association, together with the historic rotating coils and electro-dynamometer used in the determination of the B.A. unit.

Tea was served in the combination Room of Trinity College, and a majority of the visitors returned to town by the 8 o'clock express, greatly pleased with the day's outing. Others, however, prolonged their visit until Monday, and had opportunities of discussing important physical problems with the Cambridge members.

The meeting was in every sense a great success, and will long be remembered as a red-letter day in the history of the Society.

At the Science meeting held in the Cavendish Laboratory, Prof. AYRTON, F.R.S., President, in the Chair, the following communications were made:—

"Some Experiments on the Electric Discharge in Vacuum Tubes." By Prof. J. J. THOMSON, M.A., F.R.S.

The phenomena of vacuum discharges were, he said, greatly simplified when their path was wholly gaseous, the complication of the dark space surrounding the negative electrode and the stratifications so commonly observed in ordinary vacuum tubes being absent. To produce discharges in tubes devoid of electrodes was, however, not easy to accomplish, for the only available means of producing an electromotive force in the discharge circuit was by electromagnetic induction. Ordinary methods of producing variable induction were valueless, and recourse was had to the oscillatory discharge of a Leyden jar, which combines the two essentials of a current whose maximum value is enormous and whose rapidity of alternation is very great.

The discharge circuits, which may take the shape of bulbs or of tubes bent in the form of coils, were placed in close proximity to glass tubes filled with mercury, which formed the path of the oscillatory discharge. The parts thus corresponded to the windings of an induction coil, the vacuum tubes being the secondary and the tubes filled with mercury the primary. In such an apparatus the Leyden jar need not be large, and neither primary or secondary need have many turns, for this would increase the self-induction of the former and lengthen the discharge path in the latter. Increasing the self-induction of the primary reduces the E.M.F. induced in the secondary, whilst lengthening the secondary does not increase the E.M.F. per unit length. Two or three turns in each were found to be quite sufficient, and on discharging the Leyden jar between two highly polished knobs in the primary circuit a plain uniform band of light was seen to pass round the secondary. An exhausted bulb containing traces of oxygen was placed within a primary spiral of three turns, and on passing the jar discharge a circle of light was seen within the bulb in close proximity to the primary circuit, accompanied by a purplish glow which lasted for a second or more. On heating the bulb the duration of the glow was greatly diminished, and it could be instantly extinguished by the presence of an electromagnet. Another exhausted bulb surrounded by a primary spiral was contained in a bell-jar, and when the pressure of air in the jar was about that of the atmosphere, the secondary discharge occurred in the bulb, as is ordinarily the case. On exhausting the jar, however, the luminous discharge grew fainter, and a point was reached at which no secondary discharge was visible. Further exhaustion of the jar caused the secondary discharge to appear outside the bulb. The fact of obtaining no

luminous discharge either in the bulb or jar, the author could only explain on two suppositions, viz., that under the conditions then existing the specific inductive capacity of the gas was very great, or that a discharge could pass without being luminous. The author had also observed that the conductivity of a vacuum tube without electrode increased as the pressure diminished until a certain point was reached, and afterwards diminished again, thus showing that the high resistance of a nearly perfect vacuum is in no way due to the presence of the electrodes.

One peculiarity of the discharges was their local nature, the rings of light being much more sharply defined than was to be expected. They were also found to be most easily produced when the chain of molecules in the discharge were all of the same kind. For example, a discharge could be easily sent through a tube many feet long, but the introduction of a small pellet of mercury in the tube stopped the discharge, although the conductivity of the mercury was much greater than that of the vacuum. In some cases he had noticed that a very fine wire placed within a tube on the side remote from the primary circuit would present a luminous discharge in that tube.

"Some Experiments on the Velocities of the Ions." By Mr. W. C. D. WHETHAM, B.A.

In studying electrolysis, the question as to whether there is any transference of solvent when a porous wall is absent presented itself to the author. The ordinary methods of testing for transference, such as by increase of pressure or by overflow, not being available when there was no diaphragm, the author used different coloured solutions of the same salt, such as cobalt chloride in water and in alcohol, the former of which is red and the latter blue. By putting the solutions into a kind of U-shaped tube any change in the position of the line of junction of the two liquids could be measured. Two aqueous solutions in which the anion was the same were also tried, one combination being cupric chloride and common salt, and in this case the line of demarcation traversed about seven inches in three hours. The results hitherto obtained by this method agreed fairly with those found by Kohlrausch.

"On the Resistance of some Mercury Standards." By Mr. R. T. GLAZEBROOK, M.A., F.R.S.

In 1885 M. Benoit, of Paris, supplied the author with three mercury standards nominally representing the Paris Congress ohm, now commonly known as the legal ohm. Tests of these standards were described in a paper read before the Physical Society in 1885 by the present author. Recently he had occasion to compare two of the standards with the British Association coils. The mean of many concordant results gave the resistance of one of the mercury standards (No. 37) as 1.01106 B.A.U., whilst that of the other (No. 39) was 1.01032 B.A.U. Expressing them in legal ohms, the present resistances are (No. 37) 0.99986 and (No. 39) 0.99913, whilst in 1885 the values obtained were (No. 37) 0.99990 and (No. 39) 0.99917. This shows that within the limits of experimental error the ratios of the mercury standards to the B.A. coils have remained practically unchanged during six years. The numbers given above are based on Lord Rayleigh's determination of the specific resistance of mercury, which differs appreciably from that found by Mascart and other observers. Taking the mean of the later concordant determinations, the value of the mercury standards expressed in legal ohms become (No. 37) 1.00033 and (No. 39) 0.99959. The values given by the maker were 1.00045 and 0.99954 respectively, showing a very close agreement. The author also found that refilling No. 37 from the same sample of mercury produced no appreciable change in its resistance, whilst No. 39 was somewhat affected by a similar operation.

Experiments on the coefficient of increase of resistance of mercury with temperature gave the value 0.000872 as the mean coefficient between 0° and 10° C., a number rather less than that obtained by Kohlrausch.

"On an Apparatus for Measuring the Compressibility of Liquids." By Mr. S. SKINNER, M.A.

The apparatus consisted of a large spherical flask with a long narrow neck containing the liquid to be experimented upon, the lower part of which was in communication through a stop-cock and flexible tube with an adjustable reservoir. By raising or lowering the latter, the flask could be easily filled or emptied, or the quantity of liquid adjusted. The flask was enclosed in a bell-jar whose interior was in communication with a pump and barometer gauge. So sensitive was the arrangement that the compression of water produced by blowing into the jar caused the liquid to descend about 1 centimetre in the neck of the flask. This movement corresponded with a change of volume of about half a millionth. The coefficient of compressibility had been tested at different temperatures, and the results were not very different to those obtained by Tait and others. The influence of salts in solution in changing the compressibility had also been tested, and a great difference in this respect found between electrolytes and non-electrolytes.

"Some Measurements with the Pneumatic Bridge." By Mr. W. N. SHAW, M.A.

The action of the apparatus is analogous in many respects to the Wheatstone's Bridge, and its object is to compare the pneumatic resistances or conductivities of various orifices, channels, tubes, &c. The proportional arms are represented by two circular holes in thin plates of mica, the third arm by an aperture provided with a sliding shutter adjustable by a screw, and the fourth might consist of any aperture or tube whose conductivity was to be determined. The several apertures are pneumatically connected by large wooden boxes. The battery takes the form of a Bunsen burner with a long chimney, whilst the galvanometer is represented by a glass tube connecting opposite chambers and containing a vane which sets itself at right angles to the tube when no air-current is passing. The apparatus is remarkably sensitive to movements of the shutter, and on starting or stopping the draught after balance had been obtained, effects analogous to those produced by self-induction are observed. By its use it has been found that bevelling off one side of a hole in a thin plate increases the pneumatic conductivity of the aperture very considerably, particularly when the bevel is on the egress side. Another interesting result is that for square-ended tubes of given size the conductivity first increases as the length is made greater, and afterwards diminishes with further increase of length. Putting a flange on the outlet end reduces the anomalous effect, whilst a bevelled mouthpiece similarly placed causes it to disappear.

In the discussion on Prof. Thomson's paper, Prof. FITZGERALD said the beautiful experiments were likely to lead to very important results. He did not quite understand how placing a fine wire in a vacuum tube could prevent the luminous discharge, for if the wire was on the side remote from the primary, and if there was any great increase in specific inductive capacity, he would have expected the air to screen the wire.

Prof. LODGE asked for further information as to the action of the magnet in preventing the afterglow, and in some cases precipitating a luminous discharge. The experiment with the exhausted bulb within the bell-jar was also difficult to understand, and he did not see why one of Prof. Thomson's two suppositions must necessarily be true.

The PRESIDENT enquired whether Prof. Thomson had tried Mr. Crookes's experiment, in which the electric pressure necessary to produce a discharge was greatly lessened by putting a phosphorescent material in the tube.

Prof. THOMSON, in reply, said he had not tried the experiment, but the phosphorescence he had observed was of quite a different character to that produced in Mr. Crookes's tubes. To Prof. Fitzgerald he said the action of the wire was probably a question of time, and thought the whole field was in some way thrown on the wire and thus discharged. In reply to Prof. Lodge, he had not ascer-

tained the true nature of the effect of a magnet on the glow, but he believed the glow to be due to a combination which might be prevented or facilitated by the action of the magnet causing the density to be different in different parts of the bulb.

M. GUILLAUME, in discussing Mr. Skinner's paper, described the methods used by Sabine, Jamin, and others in determining the compressibility of liquids, and pointed out their defects. The chief difficulty in such experiments was in finding the compressibility of the reservoir. Numbers expressing the compressibility of mercury obtained by different observers were given, the best values varying between 0.000039 and 0.000040.

On the motion of Prof. AYRTON, seconded by Prof. RÜCKER, a hearty vote of thanks was accorded to the authors for their valuable and interesting communications, and for the kind manner in which the Society had been received and entertained by the Cambridge members.

Prof. THOMSON and Mr. GLAZE BROOK acknowledged the vote.

ROYAL INSTITUTION OF GREAT BRITAIN. *General Monthly Meeting, May 4, 1891.*

SIR JAMES CRICHTON-BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following Vice-Presidents for the ensuing year were announced:—Sir Frederick Abel, K.C.B., D.C.L., F.R.S., Sir Dyce Duckworth, M.D., LL.D., William Huggins, Esq., D.C.L., LL.D., F.R.S., David Edward Hughes, Esq., F.R.S., Hon. Rollo Russell, F.M.S., Basil Woodd Smith, Esq., F.R.A.S., F.S.A., Sir James Crichton-Browne, M.D., LL.D., F.R.S., Treasurer, Sir Frederick Bramwell, Bart., D.C.L., F.R.S., Hon. Secretary.

Professor Edmond Becquerel, F.R.S. (of Paris), Prof. Marcellin Berthelot, F.R.S. (of Paris), Professor Alfred Cornu, F.R.S. (of Paris), Professor E. Mascart (of Paris), Professor Louis Pasteur, F.R.S. (of Paris), Prof. Robert Wilhelm Bunsen, F.R.S. (of Heidelberg), Prof. H. L. F. von Helmholtz, F.R.S. (of Berlin), Prof. August Wilhelm Hofmann, Ph.D., F.R.S. (of Berlin), Prof. Rudolph Virchow, F.R.S. (of Berlin), Prof. Josiah Parsons Cooke (of Cambridge, U.S.), Prof. James Dwight Dana, LL.D., F.R.S. (of Newhaven, U.S.), Prof. J. Willard Gibbs (of Newhaven, U.S.), Prof. Simon Newcomb, F.R.S. (of Washington, U.S.), Prof. S. Cannizzaro, F.R.S. (of Rome), Prof. P. Tacchini (of Rome), Prof. Julius Thomsen, Ph.D. (of Copenhagen), Prof. Tobias Robert Thalén (of Upsal), Prof. Demetri Mendeleef, Ph.D. (of St. Petersburg), Prof. Jean C. G. de Marignac, F.R.S. (of Geneva), Prof. J. D. Van der Waals (of Amsterdam), Prof. Jean Servais Stas, F.R.S. (of Brussels), were unanimously elected Honorary Members of the Royal Institution, in commemoration of the Centenary of the birth of Michael Faraday (born 22nd September, 1791).

Charles Davis, Esq., John Douglas Fletcher, Esq., Felix Semon, M.D., F.R.C.P., Frederick Anthony White, Esq., were elected Members of the Royal Institution.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 17, April 27, 1891.

The Late M. Cahours.—This savant has left to the Academy of Sciences the sum of 100,000 francs, the

interest on which is to be distributed yearly among men who have already made themselves known by interesting work, to encourage and assist them in the prosecution of their researches, especially in chemistry. A commission of five members is to be appointed to distribute the prizes, three at least of whom must be members of the Chemical Section.

Researches on the Humic Substances.—M.M. Berthelot and André.—The substances in question are known as ulmine and ulmic acid, and for the purpose of examination have been obtained from cane-sugar. Their experiments throw a new light on the part played by humic matters in the fixation of nitrogen and of alkalis. Humic anhydride participates at once in the properties of the acid and the alcoholic anhydrides. A vacancy having occurred among the correspondents of the Section of Geography and Navigation, the Prince of Monaco received 38 votes, against 2 given to Fritjoff Mansen and 1 to Herr Schreinfurth.

Quantitative Studies on the Chemical Action of Light.—The author's results are given in formulae and tables.

Action Exerted by the Haloid Salts of Potassium on the Solubility of Neutral Potassium Sulphate.—Ch. Blarez.—The precipitating action of the potassium haloid salts upon saturated solutions of neutral potassium sulphate is proportionate to the equivalent of the salt added.

On Isocinchonine.—E. Jungfleisch and E. Leger express the opinion that Hesse's isocinchonine is not identical with cinchonine.

On a Carbide of the Terpene Series contained in the Oils of Compressed Gas.—A. Etard and P. Lambert.—The body in question, pyropentylene, $C_{10}H_{12}$, becomes polymerised in the cold. It melts at 8° , and has the specific gravity 1.0030. It is neither identical with valylene nor with perylene.

On Trehalose.—M. Maquenne.—Trehalose anhydride is an octatomic alcohol, an isomer of the saccharoses, and approximating in its constitution to maltose.

Action of Oxyhydrocarbides upon the Nitrides and Hydronitrides.—Raymond Vidal.—The action of phospham upon the alcoholic hydrates is not an isolated fact.

The Constitution of the Aqueous Solutions of Tartaric Acid.—M. Aignan.—Tartaric acid in solution in water exists as a polymer partially dissociated according to the law indicated by a discussion of the experiments of Biot.

The Artificial Production of Hyalite at Common Temperatures.—Stanislas Meunier.—Not adapted for useful abstraction.

Moniteur Scientifique, Queneville.

Series 4, Vol. iv., Part 2, No. 535.

The Part Played by Sulphur in the Metallurgy of Zinc.—F. Orgler (*Zeit. Angewand. Chemie*).—If lime is deficient each atom of sulphur keeps back an atom of zinc.

The Dismore Process for the Manufacture of Lighting Gas.—Isaac Carr.—From the *Journ. Soc. Chem. Ind.*

The Presence of Coumarone in Coal Tar.—C. Kramer and A. Spilker.—Coumarone has been obtained from the light oils of coal tar, which pass over between 175° – 178° after the phenols and the pyridic bases have been removed. The authors have also obtained from coumarone a polymer which they designate as paracoumarone.

Purification of the Heavy Oils of the Lignite Tars.—E. V. Boyen.—This paper does not admit of useful abstraction.

Considerations on the Mode of Formation of Coal and other Combustibles.—W. A. Dixon.—From the *Proceedings of the Australian Association for the Advancement of Science*.

Determination of Fatty Acids in Alizarin Oil.—F. Guthrie, Rowland Williams, and Arthur Wilson.—From the *CHEMICAL NEWS*.

New Process for the Volumetric Determination of Sulphates.—L. W. Andrews.—From the *Amer. Chem. Journ.*

Determination of Free Hydrochloric Acid in Solutions of Tin Chloride.—W. Minor (*Zeit. Angew. Chemie*).—Ten c.c. of the solution are diluted with water, and it is treated in heat with a current of hydrogen sulphide until all the tin is thrown down. The liquid is filtered and diluted to 1 litre. Of this solution 500 c.c. are taken (corresponding to 5 c.c. of the original liquid), the H_2S is expelled by boiling, and the acid is determined with a solution of soda. On the other part the tin is determined, e.g., by titration with a solution of iodine. From it we deduce the weight of the combined acid, which is then subtracted from the total acid.

The Citrate Method for the Determination of Phosphoric Acid.—O. Reitmaier (*Zeit. Angew. Chemie*).—The precipitation of P_2O_5 by the citrate method is always imperfect however the process is modified. Even in presence of lime, iron, alumina, and manganese, a compensation is possible only on using a large excess of the magnesia mixture. An excess of citrate is always necessary, and in this case the weight of the precipitate is augmented. If lime is previously eliminated there is always an error in minus if we do not use at least twice the necessary quantity of magnesia.

Reaction of Ammonium Molybdate on the Hypophosphites.—J. Millard.—From the *Pharm. Journ.*

New Process for the Volumetric Determination of Bromine in Presence of Chlorine and Iodine.—Norman McCulloch.—From the *CHEMICAL NEWS*.

Journal für Praktische Chemie.
New Series, Vol. xlii., Parts 2 and 3.

The Action of Phenylhydrazine upon the Anhydrides of Pyrocinchonic Acid, a Dichlor- γ -dimethylsuccinic Acid, and α -Dichlorpropionic Acid as well as upon the Pyrocinchonic Acid Chloride.—R. Otto and G. Holst.—The most important results of these investigations are that by the action of two mols. phenylhydrazine upon one mol. of pyrocinchonic anhydride there is first formed as an addition product the phenylhydrazine salt of pyrocinchonylphenyl hydrazinic acid, which is then further converted into β -pyrocinchonylphenylhydrazine by the abscission of one mol. each of water and phenylhydrazine. There is probably formed pyrocinchonyldiphenylhydrazide as an intermediate product. In the reaction between 3 mols. of phenylhydrazine and 1 mol. pyrocinchonchloride there is formed a pyrocinchonylphenylhydrazine along with 2 mols. phenylhydrazine hydrochlorate. In the combination of phenylhydrazine with α -dichlor- γ -dimethylsuccinic anhydride, 4 mols. of hydrazine and 1 mol. anhydride enter into reaction; and besides phenylhydrazine hydrochlorate, nitrogen and probably benzol, there is formed β pyrocinchonylphenylhydrazine. On the other hand, in the action of phenylhydrazine upon dichlorpropionic anhydride, 8 mols. of phenylhydrazine enter into reciprocal action with one mol. of the anhydride with both an allocation of the monovalent phenylhydrazine residue $-NH-NH-C_6H_5$ to the radicle of the bivalent phenylhydrazine residue $=N-NH-C_6H_5$, for both chlorine atoms, forming besides 1 mol. water and 4 mols. phenylhydrazine hydrochlorate.

Action of Chlorbenzoyl upon Sodium Cyanide in Presence of Ethyl-Ether.—W. Buddens.—Benzoyl-

chloride (1 mol.), and sodium cyanide (2 mols.), in presence of ether yield sodium benzoyl-cyanide, cyanamide, and sodium chloride. Mineral acid but not organic acids precipitate benzoyl cyanide from its salts. Benzoyl cyanide, if heated alone, is resolved into carbon dioxide, benzonitrile, and dicyandiamide. It is not polymerised if heated either alone or in liquids which boil at high temperatures. If heated with alcohols it is decomposed into the corresponding benzoic esters and cyanamide. With the exception of the silver salt its salts are readily soluble in water and in alcohol. The barium salt on heating, is decomposed into benzonitrile, carbon dioxide, and barium cyanide. Sodium cyanide (1 mol.), with chlorbenzoyl (1 mol.), in presence of ether yield as ultimate products, carbon dioxide, hydrocyanogen, benzonitrile, cyanamide, sodium chloride, dibenzoylcyanide, α -symmetric dibenzoylurea, and two isomeric bodies of the formula $(C_7H_4N_2)_x$. Dibenzoyl cyanide may also be formed directly from silver cyanide and benzoylchloride and is converted into dibenzoylurea by taking up water.

Communications from the Laboratory of the University of Freiburg.—These communications consist of a paper by Ad. Claus and Runschke on the location of the dichlorometaxylyl (4-6), obtained by direct chloration and on some of its derivatives, and a memoir by C. Willgerodt and B. Hermann on derivatives of ortho-para-dinitrophenylhydrazine.

The Influence of the Filling of Space upon the Chemical Process.—Fr. Kehrman.—This paper is not adapted for useful abstraction.

On Dimethylacetylen and its Tetrabromide.—Al. Faworsky.—The author determines the boiling-point of dimethylacetylene. At the beginning of the distillation the thermometer stood at 10° in the dephlegmator. The distillation began at 27° , and ended at 28° . The tetrabromide has the composition $C_4H_6Br_4$.

On the Geometrical Isomerism of the Bromine Derivatives of Pseudobutylene.—Al. Faworsky and C. Debout.—The authors consider that their results show that Wislicenus and Hölz have operated upon ordinary mixtures, and not upon geometric isomers.

Some Small Communications from the Laboratory of E. von Meyer.—These consist of papers by M. Schmidt on the action of sulphurous acid upon nitroso-compounds, by W. Knebel on the derivatives of salol, and by J. T. Carrick on a product of the condensation of cyanacetic ether and benzaldehyd.

Detection of Sugar or Treacle in Roasted Coffee.—A. Stutzer and O. Reitmaier (*Zeit. Angew. Chemie*).—The authors put 20 grms. of unground coffee into a litre flask, covers them with $\frac{1}{2}$ litre water, and shakes them violently for five minutes in a mechanical agitating apparatus. The flask is filled up to the mark with water, and the liquid is immediately filtered. 50 c.c. are evaporated in a platinum capsule upon the water-bath, dried for two hours at $95-99^\circ$, weighed, incinerated, and weighed again. In this manner there was obtained from pure coffee-beans from different sources from 0.44-0.72 per cent, or as the mean of five determinations 0.598 per cent. The samples when shaken up in cold water gave off no colouring-matter. Samples of coffee roasted with sugar coloured water more or less deeply, and yielded, when treated as above, 1.81-8.18 per cent of extractive matter.

Detection and Estimation of Starch in Liquids containing Dextrin.—G. Burkard (*Chemiker Zeitung*).—The cold liquid containing starch and dextrin is cautiously mixed whilst being shaken with exactly so much alcohol as to cause a slight milky turbidity. The solution is then heated until the turbidity disappears; a little solution of tannin is then added and the mixture is set cool, when all the starch present is deposited as a thin flocculent precipitate.

MEETINGS FOR THE WEEK.

TUESDAY, 26th.—Royal Institution, 3. "The Clobber Period of Stage History," by William Archer.
Institute of Civil Engineers, 8. (Anniversary).
Royal Medical and Chirurgical, 8.30.

WEDNESDAY, 27th.—Geological, 8.
THURSDAY, 28th.—Royal, 4.30.
Royal Society Club, 6.30.
Royal Institution, 3. "The Orchestra considered in connection with the Development of the Overture," by A. C. Mackenzie, Mus. Doc.
Society of Arts, 4.30. "The Study of Indian History," by C. L. Tupper, B.A.

FRIDAY, 29th.—Royal Institution, 9. "An Astronomer's Work in a Modern Observatory," by David Gill, LL.D., F.R.S.

SATURDAY, 30th.—Royal Institution, 3. "The Scientific Study of Decorative Colour," by Prof. A. H. Church, M.A., F.R.S.

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THE CHEMICAL NEWS.

Vol. LXIII., No. 1644.

ON A NEW METHOD OF MEASURING THE GLYCERIN YIELDED BY THE FATS.

By J. ALFRED WANKLYN and WILLIAM JOHNSTONE.

THE amount of glycerin given by different fats has been measured by the direct method, in which a given weight of fat is saponified, the soap decomposed by means of acid, and the glycerin extracted, purified, and finally weighed. This procedure has the advantage of conclusiveness, but it is slow and very troublesome, and is wanting in precision. There is a quicker and easier process founded upon the observation that alkaline permanganate resolves one molecule of glycerin into one molecule of oxalic and one molecule of carbonic acid. This method is of very limited applicability, inasmuch as there are many other substances besides glycerin which furnish oxalic acid on being submitted to this process of oxidation. It has, therefore, the defect of inconclusiveness, and has, we believe, led analysts into error.

There is a demand for a method of measuring the glycerin which shall have the conclusiveness of the direct estimation, and at the same time shall be rapid and precise. The method which we bring forward appears to meet these requirements.

Thirty years ago the discovery was made that glycerin and hydriodic acid react thus—



Our method takes advantage of this reaction and measures the glycerin by means of the iodide of isopropyl which it yields.

That such a method must be conclusive, if it can be worked at all, must be obvious. That it furnishes accurate results is quite practicable and comparatively quick (in one of its forms it may be completed within three hours, starting with the fat in its ordinary condition), is shown by the experiments which we have made.

ON THE GLASER OR ALCOHOL METHOD FOR THE DETERMINATION OF OXIDE OF IRON AND ALUMINA IN PHOSPHATES.

By H. H. B. SHEPHERD, F.I.C., F.O.S.

THIS method has recently been brought very prominently before the notice of English chemists by the action of the Chemical Manure Manufacturers' Association, at whose instance two influential meetings have been held for the purpose of discussing, among other subjects, the determination of oxide of iron and alumina in phosphates. At these meetings a very general opinion was expressed that, with certain modifications, the Glaser process could be recommended as a reliable and useful addition to the means at our disposal for the analysis of phosphates, and one less likely than the older method to yield inaccurate results in inexperienced hands. Exception was, however, taken to the following points, all of which form part and parcel of the method as adopted on the Continent:—

1. To working upon a solution representing so little as 0.4 grm. of phosphate.
2. To employing nitrohydrochloric acid as the solvent for the raw phosphate, and consequently including in the oxide of iron and alumina any iron present in the form of pyrites.
3. To the plan of dividing the phosphates of iron and

alumina found by 2 to obtain the oxide of iron and alumina, instead of determining the amount of the phosphoric acid in the precipitate and deducing this from the total.

As this method seems likely now to come into general practice, at any rate as an alternative one, it may be useful to those chemists connected with the manure trade who have not as yet had any experience of it to place before them some practical working details embracing modifications introduced to meet the objections referred to.

Alcohol Method.

Two and a half grms. of phosphate are dissolved in 10 c.c. hydrochloric acid, evaporated to dryness, taken up with hydrochloric acid, raised to the boil, washed out into a 250 c.c. flask with as little water as possible, 10 c.c. strong sulphuric acid added, and the solution allowed to stand for about five minutes with frequent shaking. Alcohol (95 per cent) is now added, the mixture cooled, made up to the mark with alcohol and well shaken. Owing to the contraction in volume which takes place, it must again be made up to 250 c.c. and mixed. It is now allowed to stand for one hour, filtered, 200 c.c. of the filtered solution (equal to 2 grms. of phosphate) taken, and gently evaporated to a small bulk in a basin. It is desirable when organic matter is present to carry the evaporation to pastiness, that the acid may effect its partial destruction. It is then washed into a beaker with about 50–100 c.c. water, boiled for a short time with bromine or other oxidising agent, ammonia added in excess, again boiled for about half-an-hour, cooled, a little more ammonia added to make sure a slight excess is present, filtered, washed with hot solution of ammonium chloride, ignited, and weighed. Unless ammonium chloride solution is used, the precipitate is very apt to wash through even a very close filter.

When the weight of the phosphates of iron and alumina has been obtained, the precipitate is re-dissolved and the phosphoric acid contained therein determined—the amount so found, deducted from the total weight of the phosphates of iron and alumina, giving the oxide of iron and alumina by difference. Of course, if the oxide of iron is required apart from the alumina, a separate iron determination must be made; but this, in any case, has to be done by whatever method the separation of the phosphates of iron and alumina is effected.

The following postscript has been suggested by Messrs. TSCHENMACHER and SMITH:—

Should the phosphate under examination contain *magnesia*, the phosphates of iron and alumina obtained in the foregoing process must be freed from this impurity by washing the precipitate off the filter and boiling with water and a little nitrate of ammonia, repeating the treatment if, after the first application, the filtrate still shows any *magnesia*.

ON THE PERIODIC TABULATION OF THE ELEMENTS.

By JAMES WALKER, D.Sc., Ph.D., F.R.S.E.

THE best tabular expression for the periodic law is to be found in the arrangement given by Mendeléeff, who writes the elements in periods in order of their atomic weights, and thus separates the odd from the even series by the transition elements of the eighth group. Lothar Meyer's spiral and the tables based on it do not show the relations of the elements amongst themselves to the same advantage. What is to be aimed at in such a tabulation is evidently that elements which are analogous in their chemical and other properties should be found together in the table, and apart from elements to which they bear little or no resemblance. Mendeléeff's arrangement is at

once justified by the fact that certain general statements can be made concerning the elements of odd series as contrasted with those of even series, and *vice versa*. It also, however, gives expression to generalisations of a somewhat more limited character, but still of considerable interest. In his table, here reproduced, we see, for example, that the metals of the rare earths are found together in the even series, and may be enclosed in a rectangle, as is indicated by the dotted lines in the upper part of the diagram.

EVEN SERIES.						
Group.	2.	4.	6.	8.	10.	12.
I.	Li	K	Rb	Cs.	—	—
II.	Be	Ca	Sr	Ba	—	—
III.	B	Sc	Y	La	Yb	—
IV.	C	Ti	Zr	Ce	—	Th.
V.	N	V	Nb	Di	Ta	—
VI.	O	Cr	Mo	—	W	U
VII.	F	Mn	—	—	—	—
VIII.		Fe	Ru	—	Os.	—
		Co	Rh	—	Ir	—
		Ni	Pd	—	Pt	—
I.	H	Na	Cu	Ag	Au	—
II.		Mg	Zn	Cd	Hg	—
III.		Al	Ga	In	Tl	—
IV.		Si	Ge	Sn	Pb	—
V.		P	As	Sb	—	Bi
VI.		S	Se	Te	—	—
VII.		Cl	Br	I	—	—
I.	3.	5.	7.	9.	11.	

ODD SERIES.

Again, the "metallurgical" metals are all to be found in the lower rectangle marked off in the table; and immediately adjoining these we have the technically important light metals sodium, magnesium, and aluminium, as well as the half metals arsenic, antimony, and bismuth. These relations are not clearly apparent in Meyer's table, although they come out well in his curve of atomic volumes, corresponding parts of which contain analogous elements; the metals of the rare earths, for example, lying on the lower part of the descending portions of the curve in the great periods, and the useful heavy metals at or close after the minima. In the above diagram the various periods are brought alongside each other, so that elements on corresponding parts of the curve become neighbours in the table.

One of the distinctions between elements of odd and those of even series is that only elements belonging to the former are capable of forming compounds with the alcohol radicals and with hydrogen (the transitional eighth group being here, and in what follows, left out of account). We see at once, however, that this statement is not strictly true, for the elements of the *second* series do form compounds with the alcohol radicals and with hydrogen. Again, it may be stated that the elements of even series do not occur in the free state in nature. But this also is manifestly untrue of carbon, nitrogen, oxygen, and, as it would seem, of fluorine—all members of Series 2. This exceptional position of the second series was from the first recognised by Mendeléeff, who named the elements which constitute it (and also sodium) "typical" elements. Would it not be more rational to remove Series 2 from its present position, and place it before Series 3, calling it then the first series—a name at present monopolised by hydrogen? It would thus appear amongst the odd series, and the above generalisations would apply practically without exception. By so moving Series 2, we should also be spared classifying oxygen with chromium, molyb-

denum, &c., and fluorine with manganese. The table in its modified form is given below:—

EVEN SERIES.						
Group.	4.	6.	8.	10.	12.	
I.	K	Rb	Cs	—	—	
II.	Ca	Sr	Ba	—	—	
III.	Sc	Y	La	Yb	—	
IV.	Ti	Zr	Ce	—	Th	
V.	V	Nb	Di	Ta	—	
VII.	Cr	Mo	—	W	U	
VII.	Mn	—	—	—	—	
	Fe	Ru	—	Os	—	
VIII.	Co	Rh	—	Ir	—	
	Ni	Pd	—	Pt	—	
I.	Li	Na	Cu	Ag	Au	
II.	Be	Mg	Zn	Cd	Hg	
III.	B	Al	Ga	In	Tl	
IV.	C	Si	Ge	Sn	Pb	
V.	N	P	As	Sb	Bi	
VI.	O	S	Se	Te	—	
VII.	F	Cl	Br	I	—	
	3.	5.	7.	9.	11.	

ODD SERIES.

Here oxygen is in its proper place beside sulphur; and fluorine beside chlorine, bromine, and iodine. Lithium, too, is near its analogue magnesium, beryllium near aluminium, and boron near silicon. Now, also, it can be stated that all the non-metals are in the odd series, and indeed it is possible to draw a fairly sharp line of demarcation between them and the metals. By a glance at the modified table it will be seen that all the non-metals lie in the lower left-hand corner of the diagram, and may be separated from the metals by a diagonal straight line.

The advantages gained by this modification seem to me to outweigh any slight alterations which it may be necessary to make in such rules relating to odd and even series as were laid down by the late Prof. Carnelley. The table as it stands is still far from perfect; we have still, for instance, lithium and sodium classed with copper, silver, and gold, whilst their place is evidently with potassium, rubidium, and caesium; but discrepancies such as these are much less numerous than before.

In his last paper on the Periodic Law (*Phil. Mag.*, xxix., 97), Prof. Carnelley advanced a formula which represents in a fairly close manner the atomic weight of the elements as a function of their position in the periodic system. The formula is $A = c(m + \sqrt{v})$, A being the atomic weight, m a member of an arithmetical progression depending on the series to which the element belongs, v (valency) the number of the group in which the element is found, and c a constant. After fixing the form of the expression and the numerical values in the arithmetical series, he found that the constant c was equal to 6.6, a number at once suggesting the constant 6.4 of Dulong and Petit's Law. The coincidence, however, is purely accidental. Dulong and Petit's Law expressed in corresponding algebraical form is—

$$A = c' \left(\frac{1}{\text{specific heat}} \right)$$

where c' is a constant. Now the numerical values of c and c' evidently depend on the units in which the various magnitudes in the equations are measured; and if instead of taking the atomic weight of hydrogen, and the specific heat of water at the ordinary temperature as units, we adopted some other system, then c and c' would no longer in general be even approximately equal. Thus there is no real connection between the atomic heat of the elements and Prof. Carnelley's constant, their identity depending on the form of expression chosen and the

accidental circumstance that the atomic weight of hydrogen and the specific heat of water of 18° are the most convenient units to employ in ordinary measurements of these two magnitudes.

With reference to Dulong and Petit's Law, it may not be out of place again expressly to call attention to the fact frequently overlooked, that the specific heat of the elements in the solid state is an excellent example of a property of the elements which is *not* periodic.

University of Edinburgh,
March 20, 1891.

THE ELECTROLYTIC METHOD AS APPLIED TO PALLADIUM.

By EDGAR F. SMITH and HENRY F. KELLER.

OUR knowledge bearing upon the behaviour of this metal towards the current is limited and rather indefinite. In 1868, Wöhler published in the *Annalen*, 143, 375, an article, entitled "Ueber das Verhalten einiger Metalle im elektrischen Strom," from which the following facts are taken:—Palladium, as the positive pole of a battery, consisting of two Bunsen cells, was immersed in water acidulated with sulphuric acid, when the metal immediately became coated with a deposit having a bright steel-like colour. This deposit is doubtless palladium dioxide, as it liberates chlorine when treated with hydrochloric acid, and carbon dioxide when warmed with oxalic acid. At the same time, black, amorphous metal separated upon the negative pole. Its quantity was slight. In the second edition of "Classen's Quantitative Electrolysis, p. 72 (American edition), it is stated that a feeble current will deposit palladium in a beautiful metallic state from an acid solution. One Bunsen cell is given as sufficient for this purpose. A more energetic current produces a spongy deposit. Ludwig Schucht has communicated (*Berg- und Hüttenmännische Zeitung*, 38, 121; also *Zeit. für Anal. Chem.*, 22, 240), that from an aqueous solution of palladious nitrate, acidulated with a few drops of nitric acid, the current precipitated upon the negative pole a bronze-coloured deposit, which, as it grew more dense, became darker, and finally black in colour. At the positive pole there was a simultaneous deposition of oxide, showing a reddish colour. In alkaline palladic solutions the precipitation of metal was much retarded; the deposition of oxide was also observed.

Our first experience in the electrolysis of palladium salts was acquired from the double cyanide in an excess of potassium cyanide. In such solution a current, generating 1 c.c. oxyhydrogen gas per minute, failed to cause metallic deposition until after the expiration of thirty-six hours; in other words, not until the excess of potassium cyanide had been completely converted into alkaline carbonates. Then the deposit was black in colour, but the precipitation was not at all complete. No deposition of oxide was noticed upon the positive pole. The conduct of the metal in cyanide solution led to the trial of certain separations, the results of which will be given in a later communication. The action of the current (feeble) was also tried upon a solution of palladious chloride, in the presence of a large excess of potassium sulphocyanide. In this case the deposition of metal was exceedingly rapid. Spongy spots were noticeable. The deposit was black in colour. The experiment was made with this solution in the hope that possibly a separation of copper from palladium might be found; but, as these metals separate with equal rapidity from their sulphocyanides, the results are valueless for this purpose.

The next attempt was made with palladammonium chloride, $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$, in just sufficient ammonium hydroxide to retain it in solution. The total dilution of the solution was 125 c.c.; the acting current gave 0.9 c.c. OH gas per minute. The poles were distant from each

other about two inches. Just as soon as the circuit was completed, a yellowish-brown coating appeared upon the spiral of the positive pole; while upon the dish, in connection with the negative pole, a deposit of metal closely resembling the platinum itself in colour made its appearance. After acting through the night the current was interrupted, the metal deposit carefully dried and weighed. The precipitation was incomplete. It was, however, discovered that the deposition at the positive pole, which gradually increased in mass and assumed a black colour, had entirely disappeared. In all instances where the ammonium hydroxide was in decided excess, the precipitation of oxide on the positive pole was not observed. This behaviour is similar to that of nickel when its ammoniacal solutions are electrolysed. In subsequent experiments the course was somewhat modified. From solutions such as just described, the palladium thrown out upon the platinum dish was extremely slow in dissolving, even in fuming nitric acid, so that it was deemed expedient to first coat the platinum dishes employed in the electrolysis with a layer of silver, varying in weight from 0.1 to 0.3 gm. This was done in the experiments recorded below, and was found to be decidedly advantageous. The layer of silver seemed to hasten the deposition of the palladium.

Experiment I.

A quantity of palladammonium chloride (= 0.2228 gm. Pd) was dissolved in ammonium hydroxide; to this solution were added 20 to 30 c.c. of the same reagent (sp. gr. 0.935) and 75 c.c. water. The current allowed to act upon this ammoniacal liquid gave 0.9 c.c. oxyhydrogen gas per minute. The decomposition continued through the night. At no time was there any oxide deposition upon the anode. The palladium gradually assumed a bright metallic appearance. After drying, the deposit showed about the same appearance as is ordinarily observed with this metal in sheet form. The washing was limited to hot water, and when the deposit was perfectly dry, the dish containing it was covered with a watch-glass and exposed to a temperature ranging from 110° to 115° C. This was done to expel any hydrogen that might possibly have been retained by the palladium.

Weight of silvered dish + Pd =	61.9575 grms.
" " " "	- Pd = 68.7350
	0.2225 Pd

Experiment II.

In every respect similar to Experiment I. gave—

Weight of silvered dish + Pd =	71.9540 grms.
" " " "	- Pd = 71.7315
	0.2225 Pd

The filtrates from these deposits were warmed for eight hours with ammonium sulphide without showing any formation whatever of palladium sulphide.

In several experiments, with conditions unlike those just described, and where consequently an incomplete precipitation of metal occurred, the digestion with ammonium sulphide produced in every instance, in a very short time, a reddish-brown flocculent sulphide, carrying with it quite a considerable quantity of free sulphur.

In a second series of two experiments, in each of which there was the same amount of palladium as in the previous trials, the quantity of ammonium hydroxide in excess was made 30 c.c., while the current (giving 0.8 c.c. oxyhydrogen gas per minute) was allowed to act for sixteen hours. The results were quite concordant:—

Experiment III.

Weight of silvered dish + Pd =	72.1055 grms.
" " " "	- Pd = 71.8825
Weight Pd =	0.2230

Experiment IV.

Weight of silvered dish + Pd = 62.0512 grms.
 " " " - Pd = 61.8280

Weight Pd = 0.2232

It may be remarked that in filling the silvered platinum dishes a rather large surface of silver was allowed to remain above the electrolysed liquid, so that by merely adding water it was possible to ascertain when the palladium was fully precipitated. When the deposition was not finished, the new silver surface soon showed streaks of metal.

A third series of two experiments, in which the added amount of palladium was double that recorded in the preceding examples, the same conditions were observed as before, with the exception that as the current was only giving 0.70 c.c. oxyhydrogen gas per minute, the time of precipitation was extended to eighteen hours. The results were as follows:—

Experiment V.

Weight of silvered dish + Pd = 72.3555 grms.
 " " " - Pd = 71.9100

Weight Pd = 0.4455

Experiment VI.

Weight of silvered dish + Pd = 62.2600 grms.
 " " " - Pd = 61.8138

Weight Pd = 0.4462

Curiously enough, upon warming the liquid poured off from the palladium in Experiment V., with ammonium sulphide there appeared a very slight sulphide precipitate after some hours. The liquid from Experiment VI. showed no trace of unprecipitated metal.

The deposits in the experiments just recorded were bright, metallic, and very dense. In none was there the slightest tendency to sponginess. To show the accuracy of the method, the results may be tabulated as follows:—

Experiment.	Found Pd.	Calculated Pd.
I.	0.2225	0.2228
II.	0.2225	0.2228
III.	0.2230	0.2228
IV.	0.2232	0.2228
V.	0.4455	0.4456
VI.	0.4462	0.4456

If the percentage differences be calculated, it will be found that they are quite within the limit of error occurring in almost any ordinary gravimetric determination.

The behaviour of ammoniacal palladium solutions, when exposed to the action of the electric current, will be further studied as time permits, and, if possible, the attempt will be made to re-determine the atomic weight of the metal by this method in a somewhat modified form.—*Proceedings of the Chemical Section of the Franklin Institute*, Vol. ii., 1890.

ON THE DETECTION OF MERCURY IN TOXICOLOGICAL INVESTIGATIONS.

By MARCO T. LECCO.

It is universally assumed that mercury is readily soluble in hydrochloric acid on the addition of potassium chlorate. It is also expected with certainty that in the destruction of mercuriferous organic substances by means of hydrochloric acid and potassium chlorate the entire quantity of mercury present will pass into solution. Observations made by the author during the examination of a human stomach containing mercury do not agree with this assumption.

In the stomach in question minute metallic globules could be distinctly seen, which when separated were recognised with certainty as mercury.

In order to test the stomach for other mineral poisons, and to determine the mercury it was exposed to the action of hydrochloric acid and potassium chlorate. After the destruction of the organic matter the product of the reaction was worked up in the ordinary manner. But on examining the solution it was scarcely possible to find the slightest trace of mercury. In consequence the residue which had remained undissolved in hydrochloric acid and potassium chlorate was examined more closely, when the author found that the mercury sought for had remained in the insoluble residue.

A further portion of the mercuriferous stomach was submitted to the action of hydrochloric acid and potassium chlorate. The operation was conducted in a glass dish. After a short time small globules of mercury were deposited at the bottom of the vessel, so that they were distinctly seen. After the destruction of the organic matter and the expulsion of the chlorine by heating in the water-bath, the globules of mercury remained unaltered at the bottom of the dish.

The author further convinced himself of the sparing solubility of mercury on treatment with hydrochloric acid and potassium chlorate by experiments on pure mercury. These experiments were conducted both with concentrated and dilute acid, at common temperatures with prolonged action and on the water-bath, and in all cases the result was that mercury is with difficulty soluble in hydrochloric acid and potassium chlorate.

It is, therefore, absolutely necessary in the destruction of organic matter by means of hydrochloric acid and potassium chlorate to keep this property of metallic mercury in mind, and to prolong the action of the acid and the chlorate for several hours with the application of heat and with frequent stirring.—*Berichte der Deutsch. Chem. Gesellsch.*, Vol. xxiv., No. 6, p. 928.

SEPARATION AND DETERMINATION OF NICKEL AND COBALT.

By CONSTANTIN KRAUSS.

The author re-examines the methods hitherto proposed:—

A.—Methods Founded upon the Different Behaviors of the Two Metals in their Higher Stages of Oxidation.

1. A. Jorissen proposes to oxidise the solution of the metallic salts with potassa-lye and bromine, and then to add in the cold without filtration 1 to 2 c.c. solution potassium cyanide, and then to filter. Nickel is said to pass into solution, whilst cobalt remains undissolved. Jorissen considers the method inapplicable if the nickel is in large excess. Krauss rejects the method completely, as a part of the cobalt dissolves if too much potassium cyanide is used, and if too little cyanide is employed a part of the nickel remains undissolved.

2. Terrell's method (*Comptes Rendus*, lxii., p. 139) gives quite unsatisfactory results. The separation of the cobalt as roseo-cobaltic chloride was very uncertain; the precipitate was generally very trifling, and the precipitation was never complete.

In the separation of manganese from nickel a small quantity of nickelous oxide was always carried down by the manganic peroxide.

3. M. G. Delvaux's method (*Comptes Rendus*, xcii., 723) was found to give a deficiency of cobalt which contained ponderable quantities of nickel. The precipitate of nickel was largely contaminated with cobalt, and especially with manganese.

4. G. Vortmann uses as an oxidising agent sodium hypochlorite. He takes a solution of cobalt and nickel.

containing ammonium chloride, renders it ammoniacal, and adds hypochlorite. Complete oxidation takes place even in the cold, but is more rapid at ebullition. The solution which contains the cobalt as a luteo-salt is diluted with water when cold, and the nickel is precipitated with potassa-lye as nickelous hydrate. The cobalt was always too low, and was still not free from nickel; the values found for nickel were always too high. Krauss pronounces the results as not satisfactory even for technical purposes.

5. O. Popp boils a solution of a nickelous and cobaltous salt with sodium acetate and hypochlorite in order to obtain the nickel as oxide, whilst the cobalt remains in solution. This method also was found useless.

6. W. Gibbs and H. Rose separate the two metals by boiling the neutral sulphates with lead peroxide.

Krauss after boiling for several hours with freshly prepared lead peroxide, found that ponderable quantities of cobalt remained in the solution.

7. B. Fleischer divides the solution of both metallic salts into two equal parts. After both the halves have been rendered alkaline with potassa-lye they are boiled with hypochlorite or bromine water until all escape of gas has ceased. In one of the halves the cobalt and nickel sesquioxides are filtered off, and the precipitate is added to an excess of a ferrous salt of known strength containing sulphuric acid. By titrating back with permanganate the ferrous oxide which remains unoxidised there is found the quantity of cobalt *plus* nickel. The precipitate filtered from the second half is boiled with ammonia, when all the nickel is reduced to nickelous oxide, whilst cobalt remains unchanged, and is determined volumetrically in the manner mentioned above.

In testing this method the author established the fact that in the oxidation of a cobalt salt with alkali and a hypochlorite a stage of oxidation is reached higher than R_2O_3 ; whilst the oxidation product obtained from a nickel-salt always remains below R_2O_3 . In a mixture of both metals the error may be in part compensated, and the results obtained may suffice for practical purposes.

The second part of Fleischer's process, the reduction of nickel sesquioxide with ammonia, titration of the cobalt sesquioxide, and determination of nickel from the difference, must be rejected, because an excess of cobalt is always obtained at the expense of the nickel. Besides, the reduction of nickel sesquioxide with ammonia is very slow.

8. E. Donath and Jas. Mayrhofer modify the Fleischer process by precipitating the metals in one half of the solution with potassa-lye as hydrated oxides (nickelous and cobaltous), and adding solid iodine or strong solution of iodine, whereby the cobalt is converted into sesquioxide, whilst the corresponding nickel compound remains unchanged. In the second half of the solution both metals are precipitated as sesquioxides by means of hypochlorite or of bromine water. The quantity of the sesquioxides produced is in either case obtained iodometrically.

This method also suffers from the defect that the precipitation of both metals does not yield a product of constant composition. The cobalt oxide obtained by oxidation with iodine and potassa does not answer to the formula Co_2O_3 ; but on iodometric determination yields too high results.

Experiments to obtain in one or other manner a constant oxidation product of both metals lead to a favourable result only in case of cobalt.

In this manner a determination of cobalt is easily executed. The solution is mixed with potassa-lye and hydrogen peroxide, boiled until there is no escape of gas, let cool, and a little solid potassium iodide is added. As soon as it dissolved hydrochloric acid, or preferably sulphuric acid, is added, and the vessel is well stoppered. When all the cobalt oxide is dissolved the liberated iodine is titrated with sodium thiosulphate.

9. C. Wicke precipitates the nickel sulphate with excess of potassa-lye, boiled with a copious addition of

sodium hypochlorite until the escape of gas has ceased, and hypochlorous acid can no longer be detected. A standard solution of arsenious acid is then added in excess, and heat is applied until the nickel hydroxide is again converted into the pure green nickelous hydroxide. The latter is completely dissolved by heating with tartaric acid mixed with sodium carbonate until the reaction is slightly alkaline, and the excess of arsenious acid is titrated back with normal iodine.

As in the former methods, a nickel sesquioxide of constant composition is not obtained, whence the method gives no accurate results for the determination of nickel. According to the experiments of Krauss, the method is available for the determination of cobalt, where, however, the oxidation is better effected with hydrogen peroxide.

(To be continued).

ON A NEW QUANTITATIVE SEPARATION OF MANGANESE AND ZINC.

By PAUL JANNASCH and J. F. MCGREGORY.

THE new method of separating manganese and zinc described below depends on the easy and complete conversion of the former metal into manganese hydroperoxide, whilst the zinc compounds undergo no changes. Carnot was the first who precipitated the manganic salts alone by hydrogen peroxide, and thus determined the manganese quantitatively.

As one of the writers more than two years ago made numerous preliminary experiments concerning the oxidising action of hydrogen peroxide, and has recognised it as a remarkably efficient oxidising agent in his new method for the determination of sulphur, he thought it advisable not to delay any longer to commence a series of quantitative separations by means of this reagent. The first of these separations is here communicated.

In their first experiments they set out with solutions of the mixed sulphates, acidulated with dilute hydrochloric acid (5—10 c.c.), adding a moderate excess of strong ammonia, and then effecting the precipitation with hydrogen peroxide with prolonged heating on the water-bath. Here considerable quantities of zinc oxide were invariably found accompanying the manganese precipitate. In an especial case where the manganese precipitate had been left covered upon the water-bath for more than four hours, the manganese separated was found to contain 0.0822 gm. ZnO . (The quantities taken had been 0.5380 gm. $MnSO_4 \cdot 5H_2O$, and 0.5602 gm. $ZnSO_4 \cdot 7H_2O$.) That precipitations of zinc were connected with the expulsion of the excess of ammonia appeared from the solutions filtered from the manganese precipitate, which, on concentration, soon became turbid from the separation of white flocks, which subsequently, however, re-dissolved.

When we afterwards heated on the water-bath for a very short time only (the other conditions remaining as before), the results were considerably better, so that the mean proportion of manganous oxide was found by 2.5 per cent too high, a value which could be reduced by 0.5 per cent by washing the manganese precipitate with dilute ammonia. Thoroughly satisfactory results were only obtained by considerably increasing the proportion of ammonium chloride and ammonia in the liquid to be precipitated with hydrogen peroxide, and working afterwards exactly according to the following directions—a mixture of 0.5 gm. manganese sulphate, and the same weight of zinc sulphate are placed in a Berlin-ware capsule in 75—100 c.c. water. The capsule must be large enough to hold conveniently 600 c.c. water. The solution is acidified with a little dilute hydrochloric acid, and a large quantity (at least 100 c.c.), of a solution of ammonium chloride at 15—20 per cent is added. Finally, the liquid is rendered strongly alkaline by the addition of 60—100

c.c. strong ammonia, when no brown colouration of manganic hydroxide ought to take place.

The solution thus prepared and covered with a glass capsule is at once mixed with an excess of hydrogen peroxide (50–60 c.c. free from barium chloride), and all the manganese is thus completely precipitated. It must here be noted that at the end of the precipitation the liquid suddenly boils up and spurts in consequence of the oxygen gas liberated. The precipitate thus obtained is heated for 10–15 minutes on a boiling water-bath until the precipitate settles well after stirring. It is then collected upon a roomy filter. The residue of manganic oxide adhering to the porcelain is removed from the capsule by means of a feather and rinsing with hot water and a little ammonia, and at last the precipitate is washed with boiling ammoniacal water and afterwards with hot water alone until a drop of the filtrate evaporated upon platinum foil leaves no trace of a residue. The manganese precipitate can be incinerated in a platinum or porcelain crucible without previous desiccation, and is then ignited in the blast flame until the weight is constant. A repetition of the precipitation is perfectly unnecessary. Nor is it necessary to dissolve the precipitate in hydrochloric acid and re-precipitate the manganese as a carbonate.

For the determination of the zinc in the filtrate after removal of the manganese, there is the choice of two methods. In one, the boiling ammoniacal solution is precipitated with ammonium sulphide, and the precipitate is filtered after heating for an hour on the water-bath. As the washing of the precipitated zinc sulphide involves much inconvenience it is advisable to pour through the filter only the liquid in the beaker, and then return the filter with the unwashed precipitate into the beaker which contains only small quantities of zinc sulphide. The precipitate is then dissolved in dilute hydrochloric acid with the aid of heat, and the zinc is precipitated by sodium carbonate in presence of only a small quantity of ammoniacal salt. It must be noted that zinc carbonate precipitated in this manner may contain a small impurity of silica.

In the other method the zinc solution is evaporated to dryness on the water-bath in a large platinum capsule (stirring is not necessary towards the end); the residual saline mass is heated to 125–150° in the air-bath for about an hour, and the ammoniacal salts are expelled by heating on an asbestos plate over the gas-flame. The saline masses which adhere to the sides must be occasionally pushed down to the bottom of the capsule with a stout platinum wire. An exposure of the ammonium salts directly over the flame is not admissible, as losses of zinc might possibly happen. The non-volatile residue is dissolved in hot water and a couple of drops of hydrochloric acid, the solution is filtered and precipitated at a boil with sodium carbonate in a Berlin-ware capsule.

This method of separating manganese and zinc possesses various advantages. The manganese is rapidly precipitated, and the filtration and washing are so easy that a determination of manganese in presence of zinc can be easily carried out within two hours. The weighing of the zinc does not involve any circumstantialities. These distinguishing properties of manganese precipitated with hydrogen peroxide have already induced the authors to attempt other separations in the same manner. They are already in a position to announce that manganese and nickel, and probably cobalt, can be separated in the same manner. As they are at present examining the behaviour of the alkaline potassium cyanides of cobalt, nickel, and manganese with hydrogen peroxide, they will give full reports on all these possible separations of manganese, zinc, cobalt, and nickel.—*Journ. für Prakt. Chemie*, New Series, Vol. xliiii., p. 402.

Oxides of Salts of Chrome.—M. Prud'homme.—An examination of chromium hydroxide, chloride, chlorates, and sulphites from a tinctorial point of view.—*Mon. Sci. Qués.*, No. 584.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1891.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London May 8th, 1891.

SIR,—We submit herewith the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined, the whole were found to be clear, bright, and well filtered.

Throughout the month of April the condition of the water supply to the Metropolis continued to be entirely satisfactory, in respect alike to freedom from turbidity, from colour-tint, and from excess of organic matter. Thus, in the case of the Thames-derived supply, the mean ratio of brown to blue tint was as 13·9 to 20; the mean amount of oxygen required for oxidation, 0·055 grain per gallon; the mean amount of organic carbon, 0·155 part in 100,000 parts; and the maximum amount in any single sample examined, 0·190 part in 100,000 parts of the water,—numbers which, it will be seen, correspond very closely with those recorded as expressing the results furnished by the previous month's supply.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

ON CERTAIN POINTS IN THE ESTIMATION OF BARIUM AS THE SULPHATE.*

By F. W. MAR.

In the received mode of precipitating barium as barium sulphate, three conditions are carefully observed—absence of excess of acid, slow mixing of the reagents and rest, before filtration, of twelve hours, or until the precipitate has completely subsided. Usually in this process, the precipitate is thrown out in a finely-divided, milky condition, and settles very slowly. My observation that the precipitate, under certain circumstances, is formed in a more crystalline condition and settles rapidly, led me to investigate the conditions of so rapid a precipitation. These quickly settling precipitates were noticed in the first instance, in the action of sulphuric acid upon solu-

* *American Journal of Science*, vol. xli., April 1891. Contributions from the Kent Chemical Laboratory of Yale College.—VI.

tions containing a very large amount of potassium chloride with hydrochloric acid in excess. In the course of five or ten minutes the precipitate had completely settled and was found to be in a distinctly crystalline condition, and much coarser than the usual form of precipitated barium sulphate.

At the time it was thought that the cause of this rapid subsidence was the alkaline salt present, and accordingly, a series of experiments was made in which potassium, sodium and ammonium hydroxides were added in varying amounts to about 400 c.m.³ of water, hydrochloric acid added to more than acidity (but not in measured amount), 0.5 grm. of barium chloride introduced, and precipitation brought about by adding dilute sulphuric acid. Sometimes these precipitates settled rapidly, but as often came down in the familiar milky condition. Later, another series of experiments, in which the different conditions were more carefully regulated, was made thus: in 400 c.m.³ of water were dissolved 0.5 grm. of barium chloride, 10 c.m.³ of strong hydrochloric acid, and amounts of the alkaline chlorides varying from 5 grms. to 0.05 grm., the whole being precipitated with 10 c.m.³ of a solution of sulphuric acid made by diluting the concentrated acid with three parts of water. These precipitates all settled rapidly, and the variation in the amounts of alkali seemed to exert no very marked influence. Finally, these experiments seeming to point to hydrochloric acid as the influential factor, a series of experiments was made to test the effect of varying the amount of this acid. From a solution containing in 400 c.m.³ 0.5 grm. of barium chloride and amounts of hydrochloric acid varying from 1 c.m.³ to 50 c.m.³, the barium was thrown out by means of 10 c.m.³ of dilute sulphuric acid. This series showed that the hydrochloric acid had a very marked effect upon the precipitation of the barium sulphate. When only one or two c.c. of hydrochloric acid were present, the precipitate appeared immediately, in a milky condition, and settled slowly; as the amount of acid was increased, a point was soon reached where the precipitate was not so quickly apparent, but settled out much more quickly and in a coarser condition. With 10–15 c.m.³ of strong hydrochloric acid in the solution, the precipitate settled clear in ten or twelve minutes, and was in excellent condition for filtration. When the solution contained 50 c.m.³ of the acid, the precipitate settled clear in five minutes. Upon adding the sulphuric acid to such very acid solutions, no precipitate shows for a moment, but then it separates in beautiful crystalline condition and falls almost immediately. It can be safely filtered with or without pressure in ten minutes. In one instance, in the course of the experiments just detailed, 2 grms. of barium chloride were precipitated in the presence of 30 c.m.³ of hydrochloric acid, the precipitate was allowed to settle clear, and was then filtered and washed, the whole operation being completed in seven minutes. This rapid subsidence of the precipitate is seen in hot solutions only—75° C. being the lowest temperature compatible with the attainment of good results, and 85–90° better.

To ascertain whether small amounts of barium would be precipitated in like manner from these acid solutions, a series of experiments was made with solutions containing in 400 c.m.³, 10 c.m.³ of hydrochloric acid, and 5, 10, 15, 20, 25, 30, and 50 m.grms. of barium chloride, precipitation being brought about as in the experiments above. These solutions remained clear a few minutes, and then a very transparent precipitate appeared, but in no case was it as pronounced, as the more finely-divided precipitate produced in a neutral solution containing 5 m.grms. of barium chloride by the same amount of sulphuric acid. However, by giving a circular motion to the solution in the beaker, after about 20 minutes a small conical heap of barium sulphate was collected in each case in the centre of the beaker.

Experiments were next undertaken to ascertain whether barium is completely thrown out of solution when precipitated under the conditions related above. The barium

salt used in all the experiments described below was obtained by finely powdering selected crystals of barium chloride and drying by pressure between blotting papers. Portions of the same sample were used throughout. The hydrochloric acid used was the chemically pure article of commerce and had a specific gravity of 1.20. The sulphuric acid used was obtained by diluting the pure concentrated acid with three parts of water, and had a specific gravity of 1.28.

In the first series the barium salt was dissolved in about 400 c.m.³ of water, 15 c.m.³ of hydrochloric were added, and precipitation was brought about by adding 10 c.m.³ of the dilute sulphuric acid. The precipitates were filtered, after standing about ten minutes, upon asbestos felts in perforated platinum crucibles.

	BaCl ₂ ·2H ₂ O taken. Grm.	BaSO ₄ found. Grm.	Error. Grm.
1.	0.5002	0.4760	0.0016—
2.	0.5042	0.4812	0.0006—
3.	0.5038	0.4786	0.0025—
4.	0.5002	0.4760	0.0016—
5.	0.5046	0.4812	0.0006—
6.	0.5038	0.4804	0.0006—

The results of these determinations indicate plainly a loss of barium sulphate, but inasmuch as the felts used had been made very thin and it had been subsequently observed that a small quantity of the sulphate could be collected in one of the filtrates of the series by giving a circular motion to the water, it was thought that the thinness of the felts might offer an explanation of the loss and of the varying results of the series. The following series was, therefore, made in exactly the same manner, except that care was taken to have the felts carefully made and reasonably thick.

	BaCl ₂ ·2H ₂ O taken. Grm.	BaSO ₄ found. Grm.	Error. Grm.
7.	0.5014	0.4785	0.0004—
8.	0.2227	0.2122	0.0005—
9.	0.5003	0.4773	0.0004—
10.	0.5046	0.4814	0.0004—

These results are uniform, and indicate a trifling loss only; though in the filtrates of these experiments also a very slight, but, as it proved upon re-filtering, unweighable amount of the sulphate could be collected. The precipitate in the last of these experiments was filtered off almost immediately after precipitation, and before it had completely subsided. In another case the whole operation, including the three weighings necessary, was conducted to a finish in forty-five minutes.

In spite of the appearance of the trifling deposit in the filtrate, the deficiency in barium sulphate in these determinations was not greater than should be expected from the accepted solubility of that salt in water. To ascertain the effect of strongly acid solutions upon the solubility of barium sulphate, the following determinations were made:—

In experiment 11 the same amounts of the sulphuric and hydrochloric acids, 10 c.m.³ and 15 c.m.³ respectively, were used as before, but the total volume was reduced to 100 c.m.³. In 12 and 13 the same total volume as before, 400 c.m.³, was used, but this volume contained 150 c.m.³ of the strong hydrochloric acid instead of 15 c.m.³, as in the preceding experiments.

	BaCl ₂ ·2H ₂ O taken. Grm.	BaSO ₄ found. Grm.	Error. Grm.
11.	0.5016	0.4888	0.0002—
12.	0.5004	0.4779	0.0000—
13.	0.5001	0.4776	0.0000—

It appears from these experiments that, as in the preceding series, the solubility of barium sulphate in solutions constituted as described is not increased by the free hydrochloric acid, and that the effect upon the solubility

when this acid is present in great strength is to make the precipitate rather more insoluble, if anything, than it is in water. In this connection, it should be remarked that experiments of Fresenius,* together with somewhat similar experience gained by the writer in another line of work not included in this account, point to the fact that the presence of an excess of sulphuric acid is an important condition of this high degree of insolubility. The exact amount of such excess has not been determined, but the amount used in the foregoing experiments seems to be sufficient.

In the preceding experiments barium chloride was used in considerable quantity. The following determinations were made to ascertain whether very much smaller quantities of barium would come down as completely and as soon, or whether it is necessary to let the precipitations stand longer before filtration. In these experiments the barium salt was measured from a standard solution containing 200 m.grms. of the chloride to the litre. The amounts of hydrochloric and sulphuric acids, 15 c.m.* and 10 c.m.* respectively, and the whole volume of the solution was the same as in the former experiments.

	BaCl ₂ ·2H ₂ O taken. Grm.	BaSO ₄ found. Grm.	Time in minutes between precipi- tation and filtration.	Error. Grm.
14.	0.0030	0.0024	120	0.0004—
15.	0.0050	0.0046	150	0.0002—
16.	0.0050	0.0023	5	0.0025—
		0.0043	60	0.0005—
17.	0.0050	0.0031	5	0.0016—
18.	0.0050	0.0040	10	0.0007—
19.	0.0100	0.0078	10	0.0017—
20.	0.0100	0.0085	15	0.0010—
21.	0.0100	0.0083	30	0.0012—
22.	0.0100	0.0087	60	0.0007—

From these results it would appear that the precipitation, in the presence of hydrochloric acid to the amount indicated, does not take place so rapidly when the amount of the barium salt is small, but that two or three hours are sufficient for reasonably complete separation of the precipitate in any case.

In all the experiments described above there was no attempt at a gradual admixture of the reagents, but they were measured out and at once added to the solutions, the whole being well stirred. From the results obtained it appears to be established, as regards the usual precautions in precipitating barium by means of sulphuric acid, that, contrary to former usage, it is highly advantageous to have the solution strongly acid with hydrochloric acid; that it is not necessary to add the reagents drop by drop, but that the whole quantity required to complete the reaction may be added at once; that ordinary quantities of barium salts, in presence of a considerable excess of sulphuric and hydrochloric acids, are precipitated completely and at once, but that when only a few m.grms. are present the precipitate requires more time to separate under the same conditions. Two or three hours are, however, sufficient, and in no case is the excessive time of twelve hours required.

In the light of the fact demonstrated in the preceding account, that hydrochloric acid may be introduced freely, and without detriment to the quantitative exactness of the precipitation of barium in the form of sulphate from pure solutions, it seemed desirable to look somewhat into the question as to what the influence of a large excess of hydrochloric acid might be upon the well-known contaminating effect of alkaline salts present during precipitation, especially as it is customary to attempt the purification of barium sulphate thrown down in the reverse of this process—the determination of sulphuric acid by means of a soluble barium salt—by digestion of the washed precipitate in hydrochloric acid. The following series of experiments was undertaken with this end in view. The

details are shown in the tabular statement, precipitation being effected in the presence of free acid and the alkaline salt.

	BaCl ₂ ·2H ₂ O taken. Grm.	BaSO ₄ found. Grm.	Error. Grm.	HCl in solution. C.m.*.	Alkaline salts present. Grms.
23.	0.5092	0.5032	0.0169+	110	KClO ₃ 3
24.	0.5027	0.4907	0.0107+	10	" 3
25.	0.5026	0.4944	0.0154+	100	KCl 5
26.	0.5045	0.4939	0.0122+	10	" 5
27.	0.5020	0.4931	0.0137+	10	" 5
28.	0.5013	0.4849	0.0061+	10	NaCl 5

From the results it is plain that, whatever may be the effect of digesting the washed precipitate in hydrochloric acid, the presence of this acid in large excess during precipitation in the presence of alkaline salts, does not prevent contamination of the precipitate. On the contrary, the greatest contamination seems to have occurred in those cases in which the acid was present to the largest degree, but in view of the slight variation in contamination as compared with the great differences in the amount of acid employed, it does not appear probable that the increase of acid has very much to do with the amount of contamination.

It likewise seemed to be a matter of some interest in this connection, to investigate the process by which it is currently supposed (Fres. "Quant. Anal.," vol. i., p. 547) that barium sulphate carrying alkaline salts may be effectually purified, viz., by the solution of the washed precipitate in strong sulphuric acid and re-precipitation by water. Accordingly the determinations of the following series were undertaken. The barium sulphate, precipitated from solutions containing 5 grms. of potassium chloride and 10 c.m.* of hydrochloric acid, was collected upon a filter, either paper or asbestos, and, after burning the paper or removing the precipitate from the asbestos (by tapping the crucible which held it and brushing out with a camel's hair brush), was dissolved by warming with concentrated sulphuric acid in a large porcelain crucible and, after cooling, poured into water containing 15 c.m.* to 20 c.m.* of hydrochloric acid. The water into which the solutions in strong acid was poured was warmed with a view to diminish the milkiness of the precipitate, but care must be taken to keep the temperature below 60° C. to avoid danger of spattering on the addition of the sulphuric acid. In the last two of the experiments recorded a large amount of ammonium chloride was added to the water into which the solutions in acid were poured, but this appears to be without influence upon the purification or the character of the precipitation. The precipitates, after settling clear, were filtered upon asbestos, ignited, and weighed, the original felts being employed in those cases in which asbestos was used in the first instance. Those marked with an asterisk were gathered in the first filtration upon paper, the paper being burned in the crucible in which solution of the precipitate was subsequently effected. The remainder were filtered originally upon asbestos.

	BaCl ₂ ·2H ₂ O taken. Grm.	BaSO ₄ found. Grm.	Error. Grm.
29.	0.5026	0.4746	0.0044—
30.	0.5035*	0.4830	0.0023+
31.	0.5016	0.4767	0.0024—
32.	0.5025	0.4804	0.0050+
33.	0.5046*	0.4829	0.0010+
34.	0.5004	0.4825	0.0047+

These results show, evidently, that this process of purification is not satisfactory. It is possible that the losses observed may have been mechanical, and due to the violent action of the strong acid upon the water, but the excess in weight which is noticed in the majority of the determinations can only be attributed to residual contamination.

Certain experiments, on the other hand, in which the solvent action of sulphuric acid upon barium sulphate is utilised in a different manner resulted more favourably. When a solution of barium sulphate in sulphuric acid is evaporated to dryness, the salt, as is well known, is deposited in large crystals, which can be filtered off as readily as sand. The following series of experiments show the result of an attempt to utilise this property of comparatively slow and large crystallisation in purifying the precipitate. Solution of the precipitate was effected as in the experiments described above, and the evaporation of the acid was effected over a matting of asbestos, or by means of a ring burner, in porcelain, which is preferable to platinum when the evaporation is carried on as slowly as is necessary. After the acid was completely evaporated, the crystals were washed upon a felt of asbestos, ignited, and weighed. Five grms. of potassium chloride and 10 c.m.³ of hydrochloric acid were added to the solution of barium chloride in each case.

	BaCl ₂ ·2H ₂ O taken. Grm.	BaSO ₄ found. Grm.	Error. Grm.
35.	0.5029	0.4796	0.0006 -
36.	0.5008	0.4783	0.0001 +
37.	0.5038	0.4810	0.0001 -
38.	0.5087	0.4861	0.0003 +
39.	0.5025	0.4795	0.0006 +

These results are plainly good and satisfactory so far as concerns the purification of the salt, but, when the evaporation is conducted in the manner described, several hours are needed for the evaporation, and great care must be exercised to obviate the danger of snapping which becomes manifest in the later stage of the evaporation.

By the aid, however, of a Hempel evaporating burner (*Ber. d. Deutsch. Chem. Ges.*, xxi., p. 900) the operation can be finished safely, and with but little care, in the course of half an hour. The following determinations were made exactly like those of the last series, with the exception that the evaporation was effected by means of the Hempel apparatus:—

	BaCl ₂ ·2H ₂ O taken. Grm.	BaSO ₄ found. Grm.	Error. Grm.
40.	0.5050	0.4824	0.0002 +
41.	0.5069	0.4838	0.0000
42.	0.5041	0.4825	0.0021 +
43.	0.5041	0.4812	0.0018 +
44.	0.4933	0.4801	0.0005 -

Though not an absolutely perfect process, the purification of barium sulphate by this method of solution and evaporation is evidently better by far than the old method of solution and re-precipitation by dilution.

The writer gratefully acknowledges his indebtedness to Prof. F. A. Gooch for many helpful criticisms and suggestions during the course of this investigation.

NOTICES OF BOOKS.

Bibliography of the Chemical Influence of Light. By ALFRED TUCKERMAN, Ph.D. Smithsonian Miscellaneous Collections, No. 785. Washington City, 1891, iii.—22 pp., 8vo.

DR. TUCKERMAN is already known to us as the author of valuable indexes to the "Literature of the Spectroscope," and to the "Literature of Thermodynamics," and now he places chemists and physicists under further obligations by his indefatigable zeal in bibliography. His latest production above named contains the titles of over 250 works and papers relating to the chemical influence of light; the whole is simply arranged in a few sections and alphabetically under each.

The Smithsonian Institution continues in this to pub-

lish aids for research, and to place them at the disposal of men of science. Unfortunately, however, most librarians treat the independent treatises issued by the Smithsonian Institution as if they formed numbers of a periodical, and they fail to catalogue separately the several parts of each volume of the "Miscellaneous Collections." Thus these admirable treatises are practically buried, and are less known and used than they deserve. This applies also to the "Contributions," a separate series in quarto form. The treatise before us bears the number 785, and will form part of a volume yet to be issued. Meanwhile it is available for the use of chemists and physicists interested. H. C. B.

A History of Chemistry from Earliest Times to the Present Day; being also an Introduction to the Study of the Science. By ERNST VON MEYER, Ph.D., Professor of Chemistry in the University of Leipzig. Translated, with the author's sanction, by GEORGE MCGOWAN, Ph.D., Demonstrator in Chemistry, University College of North Wales, Bangor. London and New York: Macmillan and Co.

A HISTORY of chemistry adapted to the requirements of the present day has been a desideratum in English literature. The work of Thomson is decidedly obsolete, and the treatises of Kopp and Hoefer no longer meet the wants of the student.

We therefore welcome Professor von Meyer's work, the more especially from the broad and luminous character of its views.

We no longer find here the erroneous theory that alchemy was the mother, or, as the Comteans would put it, the theological stage of chemistry. We now find it presents us merely with "a certain disjointed knowledge of chemical processes acquired accidentally," and applied "for their practical results alone, and not with the object of deducing any comprehensive scientific explanation from them."

But the earliest authentic writings touching on chemistry, such as the "Book of the Balance of Wisdom," the "Papyrus Ebers," &c., are perfectly free from the mystical gibberish of the alchemists. The alchemical period, which our author supposes as extending from at least the fourth century of our era to the first half of the sixteenth, was only incidentally contributory to the progress of the science by largely extending the area of our knowledge of chemical facts.

The next stage, according to Professor von Meyer, was the iatro-chemical, expounded by Paracelsus, Helmont, Sylvius, and their colleagues. Technical chemistry, though being ably elaborated by Georgius Agricola, was, in the author's opinion, of little influence on the prevailing tendency of the science of that age.

The author very justly considers that the history of chemistry, properly speaking, begins with Robert Boyle. He points out the general disinclination of the Ancients towards experiment and their preference for the deductive method. But we think that the mischievous influence of the Socratic school has scarcely even yet been brought into sufficient relief.

We find the destruction of the Alexandrian library still assigned to the Arabs. Both external and internal evidence seem to indicate that the sack of the Serapeion and the destruction of the library were due to Bishop Cyril.

As an instance of the untrustworthy character of the history of these times we may mention Raymund (Ramon) Lully, one of the most celebrated alchemists of the fourteenth century, and a pupil of Roger Bacon. It is not certain whether he is or is not identical with a grammarian and dialectician of the same name (*Doctor Illuminatissimus*). The most eminent chemist of this epoch was undoubtedly Basil Valentine. The history of alchemy in its later stages presents a humiliating picture. But before

looking back with pity upon the men of the seventeenth and eighteenth century we must remember that minds of the same calibre are accumulating wealth by means of "patent" medicines and systems of medical treatment.

Among the more prominent iatro-chemists we find mention of Sir Turquet de Mayerne (spoken of in old English medical works as Monsieur Mayhorn), Court Physician and, it is whispered, poisoner to James I.

The dominance and the ultimate subversion of the phlogistic theory are very clearly treated, but without the exaggerations which we encounter in the writings of Dumas and Wurtz.

The author pronounces it unjustifiable to assert that chemistry was to the end of the phlogistian period "no science," so that it was created by Lavoisier out of what was previously no science.

It is remarkable that, despite the daring assertion that "*La Chimie est une Science Française*," the doctrine of "caloric," a transformation of phlogiston, lingered long in France.

Our author speaks with just indignation of the judicial murder of Lavoisier. It would seem that whilst some of his colleagues, such as Guyton de Morveau and Monge, did not dare to offer any opposition, Fourcroy went further.

But whilst Lavoisier must be acquitted of the frivolous charges on which he was condemned, his behaviour to Scheele, Black, Priestley, and Cavendish, whose results he appropriated without acknowledgment, merits the sternest condemnation.

In the author's survey of the Lavoisierian nomenclature it is much to be regretted that the generic term "metalloids" for non-metallic elementary simple bodies should have been retained.

Passing attention must be given to the labours of a school which interfered with the healthy development of chemistry, physics, and biology in the earlier part of the century. We refer to the *Naturphilosophen*, Shelling, G. H. von Schubert, H. Steffens, Winterl, and others. This school Professor von Meyer speaks of as the "natural philosophy current of that day." "Physiophilosophy" would have been the happier term, since "natural philosophy" has in English a quite distinct meaning. Liebig complains with some bitterness that his studies under Shelling at Erlangen had cost him "two precious years of his life."

We regret that we cannot extend our survey of this most valuable and important work save by warmly recommending it to the student.

Elementary Chemistry for Beginners. By W. JEROME HARRISON, F.G.S. London: Blackie and Son.

WE are compelled to ask sorrowfully, when will authors and publishers arrive at the conclusion that elementary treatises on chemistry have been already produced in superfluity? Why this should be the case in Britain more than in other civilised countries we are quite unable to explain. But we feel convinced that, pending some capital discovery which shall demand a re-organisation of chemical science, such works, however accurate, lack a *raison d'être*. Mr. W. J. Harrison is a writer of recognised ability, and might, we submit, have employed his time and talents better.

On page 94 we find a statement which is scarcely in harmony with the latest discoveries. We are told that "plants cannot take in nitrogen directly from the air by which they are surrounded." It is now concluded that plants of the leguminous class, by means of the little nodules to be found on their roots, are able to fix and utilise atmospheric nitrogen. Hence they are not benefited by nitrogenous manures.

On the same page we find it declared that "fortunately" the sulphurous acid gas poured into the atmosphere in consequence of the consumption of pyritic fuel,

"is very soluble in water, so that every shower which falls, sweetens and freshens the air." This is perfectly correct, but every such shower inevitably moistens the trees, the ground, as well as all metal articles exposed to the weather, with a dilute solution of sulphurous acid. Under such circumstances, vegetable life quickly succumbs.

The Metallurgy of Gold: a Practical Treatise on the Metallurgical Treatment of Gold-bearing Ores, including the Processes of Concentration and Chlorination, and the Assaying, Melting, and Refining of Gold. By M. EISSLER. Third Edition, Revised and greatly Enlarged. With 187 Illustrations. London: Crosby Lockwood and Co. Small 8vo., 518 pp.

THE fact that this work has already reached its third edition since 1888 is sufficient truth that it meets a recognised want, and that it is fully appreciated among metallurgists and gold miners. The author is decidedly a practical man, with prolonged and extensive experience in California and North-Western America, and he is now engaged in studying the deposits of South Africa and the methods there in use. To the present edition there have been added four new chapters and about fifty new illustrations. Among the additional matter is an account of the Gates Rock Breaker, of the Globe Mill, which is said to be an improvement on the stamps and the Cornish rollers. Several improvements in the appliances for amalgamation and chlorination are also described. The author describes Greenwood's electrolytic method of obtaining chlorine from solutions of salt, and the successful smelting of auriferous pyrites.

Sea-Sickness: Cause, Prevention, and Cure. Voyaging for Health, with an Appendix on Ship Surgeons. A Concise Practical Treatise. By THOMAS DUTTON, M.D. (Durham). Second edition. London: Baillière, Tindall, and Cox.

THIS little work treats of a very important subject, but one which lies most distinctly outside the pale of chemical science. The author's views can be judged, favourably or unfavourably, by the practical physician only. Dr. Dutton thinks that sea-sickness "has prevented many from knowing what pleasure can be derived from a trip on the sea." But a far more important fact is the misery which it inflicts upon the multitudes who are compelled to undertake voyages for purposes of business or when emigrating. The author thinks that nothing is to be hoped from improved constructions of steamers. But it has been found possible to build vessels which aggravated the ordinary risks of sea-sickness. Such were those unhappy ten-gun brigs, one of which, the notorious "Beagle" was thought good enough for a scientific exploring expedition, and rendered Charles Darwin an invalid for life. How little the tendency to sea-sickness is overcome even in seafaring life may be gathered from the author's own experience, no less than from that of Lord Nelson. Dr. Dutton seems to hold that if there is a specific for sea sickness it is ammonium bromide taken regularly for some days before going on board.

A somewhat distinct subject is the very unsatisfactory position in which the ship's surgeon is placed. If he does his duty he becomes a "black sheep" and imperils his position. The author thinks that the surgeon should be perfectly independent of the captain. He thinks that the Board of Trade should form a medical marine department, and should make the appointments. It is said—and, we believe, with too much truth—that many captains and owners like incompetent, idle surgeons, as they give no trouble and never write to the Board of Trade. This, however, is a subject which belongs to medical authorities. It is curious that whilst on railways the wide distinction which formerly existed between the first class

and the third class passenger in fading away, on passenger steamers the movement is in the contrary direction. Invention is racked to find increased luxuries for the first class, whilst the third class are treated little better than convicts, and are denied even that ordinary civility which is generally considered a cheap boon.

CORRESPONDENCE.

ELECTROLYTIC ASSAY OF COPPER.

To the Editor of the Chemical News.

SIR,—Happening to look over some back numbers of the CHEMICAL NEWS, I notice a query by an inquirer who signs himself "Deposit" on "Electrolytic Assay of Copper" (CHEMICAL NEWS, vol. lxii., p. 25). Having had the same trouble as your inquirer has had, I think it may perhaps relieve him to know he is (or was) suffering from a current which was too strong for the solution; with a weaker current of electricity, and also possibly a weaker solution of the copper, the deposit on the cathode would be firm, and either shiny or of a rosy appearance. —I am, &c.,

JOHN RUFFLE.

Rape Oil.—Reimer and Will (*Deutsch. Chem. Gesell.*).—According to the authors, rape oil consists of the glycerides of three distinct fatty acids, one of which, melting at 75°, occurs only in very small quantities. The other two, erucic acid and a liquid acid which the authors name rapinic acid, are present in equal quantities. Lead erucate is readily soluble in hot ether. The zinc salts of the fatty acids can be separated by means of ether.

Detection of Cotton Oil in Lard.—A. Bujard and J. Waldbauer (*Zeit. Ange. Chem.*).—The authors use Bechtholder's silver nitrate test and Labiche's lead acetate reaction. For the former test 10 grms. of the filtered anhydrous lard are heated with 5 c.c. of silver nitrate solution (1 part silver nitrate, 200 alcohol, 40 ether, and 0.1 part nitric acid) in the water-bath for fifteen minutes, shaking continually. The mixture, according to its proportion of cotton-seed oil, turns more or less deeply reddish brown to black. Pure lard, poppy, olive, and sesame oils are not affected. For the Labiche test, 25 grms. of the clear melted sample are mixed with a 25 c.c. of a solution of lead acetate, heated to 35°, and well mixed after the addition of 5 c.c. ammonia. The emulsion thus obtained, if cotton oil is present, soon shows a yellowish red colour, which becomes more intense after standing for a day. Poppy-rape, sesame oils, and pure lard are not affected.

Determination of Resin Oil in Mineral Lubricants.—L. Storch (*Chemiker Zeitung*).—10 to 15 grms. of the lubricant containing resin oil, but no fatty oils, is gently heated on the water-bath in a small flask with 5 vols. alcohol at 96 p.c., shaken up, and let cool down to the temperature of the room. The alcohol is then placed in a small Erlenmeyer flask about 7 cm. in height; the mineral oil which remained in the first flask is rinsed round (not shaken) with a few c.c. of 90 per cent alcohol, the solution poured into the second flask and heated upon a water-bath which is slightly simmering, enclosing it within a beaker with the bottom cut off to avoid too rapid condensation on the sides of the vessel. The heat is continued until the residue in the flask is free from bubbles. It is weighed when cold, and the residue is covered with ten parts by weight of alcohol at 96 per cent. If the residue consists entirely of resin oil this quantity of alcohol will suffice for its solution. The alcoholic solution is treated as above, and the residue contains small quantities of mineral oils.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxii., No. 18, May 4, 1891.

Quantitative Studies on the Chemical Action of Light. Reactions with Different Thicknesses and Different Forms of Vessels.—George Lemoine.—This memoir does not admit of useful abstraction.

Certain Compounds Formed by Mercuric Chloride.—G. André.—The author has obtained double zinc and mercury ammonium chlorides by dissolving in ammonium chloride either the two oxides or an oxide and a chloride. Aniline also acts upon mercuric chloride, giving, like ammonia, two kinds of compounds—the first, a well-known addition compound, $C_6H_5(NH_2)_2HgCl_2$, and the second a substitution compound, $C_6H_5NH_2 \cdot HgCl$. With benzylamine the results are more definite.

Announcement of a General Law determining as a Simple Function of the Chemical Constitution of Bodies the Temperatures of their Changes of Conditions under all Pressures.—G. Hinrichs.—A purely mathematical paper.

On Boron Selenide.—Paul Sabatier.—The author has succeeded in obtaining this compound by causing vapours of selenium or a current of hydrogen selenide to pass over amorphous boron heated to redness. Boron selenide is less fusible and volatile than the corresponding sulphide. Its odour is exceedingly irritating.

On the Action of Hydriodic Acid upon Boron Bromide.—A. Besson.—The compounds produced are the bromiodide, BBr_2I —a colourless liquid distilling about 125°; and $BBrI_2$, also a colourless liquid which distils about 180°.

On Basic Magnesium and Zinc Chromites and on Neutral Cadmium Chromite.—G. Viard.—The author has obtained magnesium chromite, $2MgOCr_2O_3$, by calcining magnesium chromate. At higher temperatures there is formed $MgOCr_2O_3$. By the action of potassium bichromate upon magnesia there is obtained an intermediate product, $3MgO, 2Cr_2O_3$. The action of alkaline chromates upon magnesium chloride does not seem to furnish pure products. The calcination of zinc chromate yields a violet-black compound, $3ZnO, 2Cr_2O_3$. Cadmium gives results much less complex than do magnesium and zinc, producing only one compound, CdO, Cr_2O_3 .

Preparation of Disodium Erythrate.—M. de Forcrand.—It results from these researches that whilst we may easily replace the first and second equivalent of alcoholic hydrogen of erythrite by sodium, the two others resist this action even in presence of an excess of soda.

Formation of Dimethylacrylic Acid in the Preparation of the Acid Amides of Isovaleric Acid.—E. Dunliet.—In preparing the amidic acids of isovaleric acid the author has followed the ordinary method, which consists in calling bromoisovaleric acid to react upon an ammonia. But after having decomposed the ammoniacal salts of baryta, expelled the ammonia by ebullition, and precipitated the baryta by sulphuric acid, in place of setting the amidic acid at liberty by silver oxide, he previously submitted the liquid to distillation. He collected an acid product which, after saturation with soda, evaporation to dryness, and treatment with sulphuric acid, yielded a notable quantity of an oily acid, very sparingly soluble in water, distilling at 175–195°, absorbing bromine and iodine and partly crystallising. The crystals have the composition and the properties of dimethylacrylic acid.

Discussion of the Experiments of Biot relating to Aqueous Solutions of Tartaric Acid in Presence of Potassa or Soda.—M. Aignan.—This memoir does not admit of useful abstraction.

Methylmethylecyanosuccinate; Methylethenyltricarboic Ether.—L. Barthe.—The author, under a pressure of 0.06 m.m., and at a temperature of 195–200°, obtains a homogeneous, colourless, oily liquid, the composition of which may be expressed by the formula $C_8H_4NO_4$.

Moniteur Scientifique, Quasneville.
Series 4, Vol. iv., Part 2, No. 584.

Camille Kœchlin.—P. Schutzenberger.—An obituary notice of the illustrious tinctorial chemist of Mulhouse, followed by a list of his researches.

The Chemical Revolution.—M. Lavoisier.—An abstract of M. Berthelot's paper compiled by Hippolyte Stupuy. We can merely quote the epigrammatic utterance of Lagrange: "It took them (the terrorists), merely a moment to cause this head to fall, but a century will perhaps not suffice to produce such another."

On Beer-Yeast.—H. Bungener.—This paper requires the ten accompanying figures.

Action of Mineral Acids in Saccharification by Malt, and in the Fermentation of Starch.—Dr. J. Effront.—A detailed study of the action of hydrofluoric acid, and of the soluble fluorides, upon diastase upon yeast, and upon the fermentation of solutions of cane sugar and of worts. The industrial use of the fluorides in distilleries has been made the subject of a Belgian patent.

MISCELLANEOUS.

Royal Institution.—An extra evening meeting will be held on Tuesday, June 2nd, at 9 o'clock, when Dr. Chas. Waldstein will give a discourse on "The Discovery of the 'Tomb of Aristotle.'"

Institution of Naval Architects.—At a meeting of the Council of the Institution of Naval Architects held on the 15th inst., it was unanimously resolved to award the Gold Medal of the Institution to Prof. V. B. Lewes, F.C.S., F.I.C., for his paper on "Boiler Deposits," read at the recent Annual General Meetings of the Institution.

MEETINGS FOR THE WEEK.

MONDAY, JUNE 1ST.—Society of Chemical Industry, 8. "Gum Arabic and its Modern Substitutes," by Dr. S. Rideal and W. E. Youle. "On the Quantitative Analysis of Light and Colour, founded on the Tintometer Colour Scales," by J. W. Lovibond.

TUESDAY, 2ND.—Royal Institution, 3. "The Garrick Period of Stage History," by William Archer.

THURSDAY, 4TH.—Royal, 4.30. Royal Institution, 3. "The Orchestra considered in connection with the Development of the Overture," by A. C. Mackenzie, Mus. Doc.

Chemical, 8. "Observations on the Molecular Refraction and Dispersion of Various Substances in Solution," by Dr. J. H. Gladstone, F.R.S. "The Nature of Solution as Elucidated by a Study of the Densities, Heat of Dissolution, and Freezing-points of Solutions of Calcium Chloride," and "A Reply to a Recent Criticism of the Conclusions drawn from a Study of Various Properties of Sulphuric Acid Solutions," by S. U. Pickering, F.R.S. "On Volatile Platinum Compounds," by W. Pullinger.

FRIDAY, 5TH.—Royal Institution, 9. "On the Discovery of the 'Tomb of Aristotle,'" by Charles Waldstein, Ph.D. Quekett, 8.

Geologists' Association, 8. SATURDAY, 6TH.—Royal Institution, 3. "The Scientific Study of Decorative Colour," by Prof. A. H. Church, M.A., F.R.S.

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AND
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THE CHEMICAL NEWS.

Vol. LXIII., No. 1645.

THE WAR AGAINST CRAM.

It is very satisfactory to find that the protest against "cram" in education, which was so ably and forcibly raised by Mr. Auberon Herbert, is not being allowed to die out. We therefore take the opportunity of meeting some of the pleas still urged in favour of examinationism.

Says a contemporary, the prospect of the abolition or the mitigation of the present tests is exciting the hopes of students. This is a complete misapprehension. No idle or incompetent youth will find degrees and honours easier of attainment. If the new movement is successful the very contrary will be the case. Nothing but sterling work—successful research in some department of science or literature—will open the gate to the candidate. Our senior wranglers, double first men, Fellows of colleges, &c., will be the men who have proved themselves able to make some addition to the existing sum total of human knowledge. They will emphatically not be the men who prove themselves the most apt in re-absorbing and re-producing—however intelligently—the knowledge of others. They will not be mere "secondary batteries," which, when charged, merely give off what has been put into them with a certain percentage of loss. Without any wish to be offensive, we cannot help saying that the emptier a vessel the greater is its receptive power. This fact, in its bearing upon their pupils, is not overlooked by university "coaches." "Such a one," said a member of this prosperous and influential fraternity, "would do very well, only he thinks!" Now we wish to bring to the front a quite different class of men from those who now take honours, men who cannot be easily crammed because their mental condition is that of a plenum, not a vacuum, men of suggestive fruitful minds, full of resources, as distinguished from mere walking text-books.

We must never forget that in the country which is our most formidable rival in science, pure or applied, examination plays a very slight part, and competition no part at all. If we look through its copious scientific literature we note the total absence of books compiled for the use of students preparing for one or the other examination, or adapted to some newly-devised syllabus. The German professor aims at qualifying his students, not to "pass," but to know. His reputation rises with the number of successful researches conducted in his class-rooms. Now it is self-evident that before a student can do good work in any science, he must be well grounded in the general laws of such science, and be more particularly acquainted with all that has been done in the subject he takes in hand.

This method of teaching any science—say chemistry—by leading the student as rapidly as possible into the fields of original research, is not an untried experiment, but a method which has been successfully adopted on the largest scale.

When a man has once shown himself capable of conducting a research, we cannot be mistaken as to his intellectual calibre. But by no examination yet devised or even conceivable can we gauge his power of accurate and thorough observation, and of drawing right conclusions from the facts ascertained. The examiner may find out what a student *knows*, but not what he can *do*. The coach may convey into his memory information without end, but he cannot give the pupil mental resources. Hence examinations really tell us little as to the value of a candidate. We have heard it said that the ability to

play a good game of whist is in reality a better test than any which the Civil Service Commissioners have invented.

EARLY STUDIES ON THE METALS OF THE RARE EARTHS.

It is not generally known in this country that one of the earliest workers in this interesting and delicate department of analytical chemistry was H.I.H. Prince Louis Lucien Bonaparte. We have recently received from the author a copy of a pamphlet, reprinted from the *Gazzetta Toscana della Scienza Medicofisica* of April 15th, May 1st, and September 1st, 1843, containing articles by H.I.H. on the rare earths.

Although half a century has thus elapsed since the publication of these researches, we think that their reproduction will be found not merely of historical interest, but even suggestive for chemists engaged in such investigations.

The subjects more particularly discussed in the pamphlet before us are the separation of cerium from didymium by means of the action of valerianic acid upon the mixed nitrates. He obtained didymium oxide so free from cerium that no trace of cerium could be detected in the concentrated and neutralised solution. He further finds that benzoic acid is quite as effective for the separation of cerium and didymium as is valerianic acid, cerium benzoate being precipitated, whilst the didymium salt remains in solution in the acid liquid. The author suggests, also, the use of phocenic or of butyric acid, but points out that they would present no advantage except from an economical point of view. He shows that the substance, which at that time was generally regarded as cerium sesquioxide, obtained by calcining the nitrate, is a mixture of cerium, didymium, and lanthanum oxides.

The pure cerium dioxide, as obtained by Prince L. L. Bonaparte, is described as insoluble in dilute acids and not easily soluble even in concentrated and boiling acids. If didymium or lanthanum is present it is more soluble. It is light yellow in colour, without any approach to a brick-red, and if finely triturated it becomes nearly colourless. The salts and the hydrate are yellow. The hydrate dissolves in nitric acid, and the solution, if prepared in the cold, is not rendered turbid by a further addition of nitric acid. If the solution is rendered perfectly neutral and boiled, it becomes turbid, and deposits an isomeric nitrate, insoluble in acidulated liquids, but soluble in pure water. The author puts on record that the solution of this salt becomes very turbid on the addition of a solution of potassium sulphate.

The pure cerous salts were found colourless and not precipitable by the valerianic, benzoic, or succinic acid, as are the ceric salts. They are precipitated by oxalic acid and with potassium sulphate. They form the well-known double sulphate.

On carefully reading this pamphlet we are led to the belief that, had the Prince been able to continue his studies with a larger supply of material, and, above all, with the spectroscope at command, he would have anticipated much that has since been done by others.

In one sense we are happy to learn that the illustrious author has supplemented the philological studies in which he has achieved so much by a return to the science of chemistry. Still we must all regret the immediate occasion—the necessity for economising his failing eyesight.

Thermic Data on Propionic Acid and the Potassium and Sodium Propionates.—G. Massol.—Propionic acid, when combining with potassa and soda, liberates as much heat as its higher and lower homologues—the acetic and the butyric acids.—*Comptes Rendus*, cxlii., No. 20.

SEPARATION AND DETERMINATION OF
NICKEL AND COBALT.

By CONSTANTIN KRAUSS.

(Continued from p. 255).

10. P. Gucci (*Gazz. Chim.*) evaporates the solution of both metals to dryness, heats the residue with saltpetre until it is in quiet flux, takes up in warm water, filters, and washes with hot water. The residue is rinsed into a beaker, the chief part of the water is poured off, and mixed with double its volume of nitric acid at 1.2 sp. gr. The beaker is then plunged for a minute into boiling water, let cool, and the contents are filtered. All the nickel is said to be in the filtrate, whilst the cobalt oxide remains undissolved.

This method does not effect a complete separation of the two metals. The result is too much nickel and too little cobalt.

11. H. Rose (*Handb.*, 6th edition) mixes the neutral solution of the metals with hydrochloric acid, and passes into the strongly diluted liquid chlorine gas until it is completely saturated. Recently precipitated barium carbonate is then added in excess, and the mixture is allowed to stand in the cold for twelve to eighteen hours, with frequent shaking. The cobalt is supposed to be separated as cobaltic hydroxide, whilst the nickel remains in solution. Henry proposes the use of bromine-water in place of chlorine, and Denham Smith recommends a solution of chloride of lime, which has been completely decomposed by the addition of sulphuric acid.

According to the author, this method gives approximately satisfactory results if it is carried out according to Henry's modification and with the aid of refrigeration. The cobalt oxide eliminated contains then in most cases merely a trace of nickel, which is scarcely ponderable. But the results are quite useless if the experiments are made at the ordinary temperature of the work-room. If the solution is heated all the nickel is deposited as a blue-black oxide.

12. Liebig (*Annalen der Chemie*) mixes the solution of the two metals with hydrochloric acid in decided excess, and adds potassium cyanide until the precipitate of nickelous and cobaltous cyanides formed is re-dissolved. A little more potassium cyanide is then added and the liquid is boiled for some time, adding gradually hydrochloric acid, but not in such a quantity that the reaction becomes acid. The liquid is then boiled in a flask with an excess of hydrochloric acid until, on a further addition of hydrochloric acid, no escape of hydrocyanic acid can be traced. The cobaltous cyanide passes into the state of a cobaltic cyanide, whilst the nickelous cyanide is decomposed with a formation of nickelous chloride. The nickel can then be precipitated with potassa-lye and determined as nickelous oxide. The filtrate is evaporated to dryness with nitric acid, and the residue is fused for a considerable time in a porcelain crucible. On treatment with hot water cobaltic oxide remains undissolved.

According to H. Rose, this method gives accurate results if carefully executed, but is inferior to the process with chlorine gas (No. 11).

Krauss contests this opinion, as, according to his experiments, if a sufficient quantity of potassium cyanide is used and the ebullition duly prolonged with a very gradual addition of hydrochloric acid, Liebig's method gives decidedly better results than that of Rose. The cobaltic oxide separated from the melt requires, however, as Rose observes, to be re-dissolved and again precipitated.

Liebig modifies his method as follows:—The solution of the metallic salts is mixed with hydrocyanic acid and potassa-lye and heated until everything is dissolved. After the excess of hydrocyanic acid has been expelled by boiling, the nickel (present as nickelous cyanide) is separated with elutriated mercuric oxide, partly as nickelous

oxide and partly as cyanide. The cobalt, which is present as potassium cobalticyanide, remains in solution, and can be precipitated from the filtrate (after acidulation with acetic acid) as copper cobalticyanide by the addition of copper sulphate. The precipitate is decomposed with potassa-lye, and the quantity of the cobalt is calculated from that of the copper oxide separated out. If it is thought preferable to determine the cobalt directly the precipitate of copper cobalticyanide after ignition is dissolved in hydrochloric acid, with the addition of a few drops of nitric acid, the copper is precipitated with hydrogen sulphide, and the cobalt is determined in the filtrate according to one of the well-known methods.

This modification gives surprisingly accurate results if the directions are accurately followed, and if the ebullition is sufficiently prolonged. But the precipitation of the cobalt with copper sulphate cannot be recommended, since the precipitate, as Rose has observed, either becomes slimy and retains potassa, or is so finely crystalline that a clear filtrate cannot be obtained.

Wöhler has simplified Liebig's method. After precipitating the nickel with mercuric oxide he neutralises the solution with nitric acid, precipitates mercury cobalticyanide by means of mercurous nitrate, ignites the precipitate strongly, and determines the residual cobalt oxide in the known manner.

With this modification Krauss obtains very satisfactory results. For determining the cobalt in the mercury cobalticyanide the following volumetric process was found very advantageous:—The precipitate, which has been previously heated with dilute nitric acid, is decomposed with alkali, free from any haloid, and the black mercurous oxide is filtered off. The filtrate is supersaturated with nitric acid, a measured quantity of a standard solution of silver is added, and the excess of silver is determined in the filtrate by Volhard's method with ammonium sulphocyanide and iron-alum.

(To be continued).

THE PRICE OF HIGH CLASS PHOSPHATES.

By ALEX. BUCHAN, F.I.C.

THESE are usually sold at so much per unit, with a rise of, say, one-fifth of a penny per unit for each unit over, say, 70 per cent, calculated on the dry sample, and an allowance of 2 units of phosphate for each excess unit of iron and alumina over, say, 4 per cent after the unitary price has been fixed.

These terms are very unfair to the manufacturer, and with the object of drawing their attention to the subject this article has been written.

The percentage is calculated on the dry sample. Now this may be fair enough in the case of rock phosphates, which require to be dried anyway before grinding, but it is manifestly unfair in the case of ground phosphates, like Somme, which sometimes contain as much as 5 per cent moisture.

It is weighed and delivered in the moist state and used without any drying, so why introduce an altogether foreign element into the question, and raise the price but certainly not the value something like 4 per cent? If the seller wants to be paid on the dry sample let him deliver it in this more valuable condition.

The allowance for iron and alumina is made after the unitary price has been fixed. Now it is quite evident that the iron and alumina reduce the value, else why the allowance of 2 units of phosphate for each excess unit? Consequently the allowance should be made before the unitary price is fixed. The present regulation seems to show that the iron and alumina do not reduce the value of each unit, but only the number of them, which is absurd.

An example will make this contention clearer:—

100 tons Somme phosphate, testing—

Phosphate of lime		80 per cent
Iron and alumina		6 "
Moisture		5 "

at 12 pence per unit on 70, rising $\frac{1}{2}$ d., calculated on the dry, with an allowance of 2 units of phosphate of lime for each excess unit of iron and alumina over 4 per cent,

The dried sample would test—

Phosphate of lime	..	84.21 per cent
Iron and alumina	..	6.31 "

The seller's way of invoicing this would be—

Phosphate delivered		100 tons
Less 5 per cent for moisture		5 "

95 "

84.21 units - 2 (6.31 - 4) = 79.59 units.

at 12 + $\frac{1}{2}$ (84.21 - 70) = 14.84 pence per unit.

79.59 units at 14.84 pence $\times$ 95 tons = £467 10s.

The fair and just way would be—

80 - 2 (6 - 4) = 76 units at 12 + $\frac{1}{2}$ (76 - 70) = 13.2 pence per unit.

76 units at 13.2 pence $\times$ 100 tons = £418.

A difference of 10 per cent against the seller.

Laboratory,
Port Dundas Chemical Works,
Glasgow, May 18, 1891.

ON THE BASES (ORGANIC) IN THE JUICE OF FLESH. PART I.*

By GEORGE STILLINGFLEET JOHNSON,
M.R.C.S., F.C.S., F.I.O.

THE author has endeavoured to ascertain by careful experiments how far the substances hitherto prepared from flesh are true "educts," and really present in the flesh itself, or merely products, due to (1) the action of chemical or physical agencies applied in the course of extraction, or (2) to bacterial action modifying the composition of the flesh before it comes into the hands of the operator.

Preliminary experiments are first described bearing chiefly upon the first-named source of error.

Liebig's process for extracting kreatine from the juice of flesh was modified by omitting the use of baryta-water, with the result that abundance of kreatine was obtained, mixed with acid potassium phosphate (KH_2PO_4). In Liebig's process potassium chloride is obtained after the kreatine has been separated.

A preliminary experiment has been described in which the author precipitated the albumenoid matters from the watery extract of fresh butchers' beef by means of solution of mercuric chloride, the filtrate depositing on standing a spherical precipitate, consisting of the mercuric salt of the sarcous kreatinin, from which a tabular kreatinin was obtained isomorphous with the tabular kreatinin obtained by the author from human urine in 1887.

The special advantages of the method adopted by the author in isolating the kreatinin of urine are next detailed, after which a series of experiments are described in which muscle substance in different stages of freshness was extracted with water, the extracts treated by the mercuric chloride method, and the products compared.

Among these products is sarcous kreatinin, whose properties are fully described and carefully compared with those of urinary kreatinins previously investigated (vide *Roy. Soc. Proc.*, vol. xliii., pp. 493-534).

The final conclusion drawn is that sarcous kreatine is not present in fresh muscle, but results from bacterial action, whereas sarcous kreatinin is probably a true "educt."

JUSTUS VON LIEBIG: AN AUTOBIOGRAPHICAL SKETCH.*

[At the recent celebration of the Jubilee of the Chemical Society, reference was made to the wonderful energy and ability of Liebig, to the great work which he did in founding organic chemistry, and to the immense stimulus which he gave, alike in his own country and in England, to scientific investigation in pure chemistry and in its applications to agriculture, physiology, and pathology.

Very opportunely a portion of an autobiographical sketch in Liebig's own handwriting has just come to light, in which he gives a most interesting account of the formation of his habits of thought, and of the development of his scientific activity. He also gives an amusing description of the lectures given in his student days by professors of the deductive method.

In his sixtieth year, we are told, Liebig wrote some biographical sketches which were laid aside and could not be found when he wished to resume them. They were never finished. A portion of the manuscript was found among some other papers in Liebig's handwriting by his son Dr. Georg Baron von Liebig, and has been published by the latter in the *Deutsche Rundschau* for January, 1891. Mr. E. K. Muspratt has been good enough to lend me a copy which he received from his friend the present Baron.

I have endeavoured to render it into English as literally as the difference in the idiom and modes of expression in the two languages will permit; and it is now made public in England by the kind permission of the *Deutsche Rundschau*.

His method of teaching and its remarkable success are worthy of attention at the present time, when technical education is occupying so much of the public mind.]

My father, who had a colour warehouse, frequently occupied himself in making some of the colours in which he dealt, and for that purpose had fitted up for himself a small laboratory to which I had access, and where I sometimes enjoyed the privilege of helping him. He made his experiments as prescribed in works upon chemistry, which were, with great liberality, lent to the inhabitants of Darmstadt from the rich Court Library.

The lively interest which I took in my father's labours naturally led me to read the books which guided him in his experiments, and such a passion for these books was gradually developed in me that I became indifferent to every other thing that ordinarily attracts children. Since I did not fail to fetch the books from the Court Library myself, I became acquainted with the librarian Hess, who occupied himself successfully with botany, and as he took a fancy to the little fellow, I got, through him, all the books I could desire for my own use. Of course the reading of books went on without any system. I read the books just as they stood upon the shelves, whether from below upwards, or from right to left was all the same to me; my fourteen-year-old head was like an ostrich stomach for their contents, and amongst them I found side by side upon the shelves the thirty-two volumes of Macquer's "Chemical Dictionary," Basil Valentine's "Triumphal Car of Antimony," Stahl's "Phlogistic

* Abstract of a Paper read before the Royal Society, May 28, 1891.

* Read at a joint Meeting of Societies in the Chemical Laboratories, University College, Liverpool, on Wednesday evening, March 18, 1891, by Prof. J. Campbell Brown, D.Sc.

Chemistry"—thousands of essays and treatises in Göttling's and Gehlen's periodicals, the works of Kirwan, Cavendish, &c.

I am quite sure that this manner of reading was of no particular use so far as acquisition of exact knowledge is concerned, but it developed in me the faculty, which is peculiar to chemists more than to other natural philosophers, of thinking in terms of phenomena; it is not very easy to give a clear idea of phenomena to anyone who cannot recall in his imagination a mental picture of what he sees and hears, like the poet and artist for example. Most closely akin is the peculiar power of the musician, who, while composing, thinks in tones which are as much connected by laws as the logically arranged conceptions in a conclusion or series of conclusions. There is in the chemist a form of thought by which all ideas become visible to the mind as the strains of an imagined piece of music. This form of thought is developed in Faraday in the highest degree, whence it arises that to one who is not acquainted with this method of thinking, his scientific works seem barren and dry, and merely a series of researches strung together, while his oral discourse when he teaches or explains, is intellectual, elegant, and of wonderful clearness.

The faculty of thinking in phenomena can only be cultivated if the mind is constantly trained, and this was effected in my case by my endeavouring to perform, so far as my means would allow me, all the experiments whose description I read in the books. These means were very limited, and hence it arose that, in order to satisfy my inclination, I repeated such experiments as I was able to make a countless number of times, until I ceased to see anything new in the process, or till I knew thoroughly every aspect of the phenomenon which presented itself. The natural consequence of this was the development of a memory of the sense, that is to say of the sight, a clear perception of the resemblances or differences of things or of phenomena, which afterwards stood me in good stead.

One will easily understand this if one imagines, for instance, a white or coloured precipitate which is produced by mixing two liquids; it is formed either at once or after some time, it is cloudy or of a curdy or gelatinous character, sandy or crystalline, dull or bright, it deposits easily or slowly, &c.; or if it is coloured it has a certain tint. Among the countless white precipitates each has something peculiar to itself; and when one has experience in this sort of appearances, whatever one sees during an investigation at once awakens the remembrance of what one has seen. The following example will make clear what I mean by sight or eye memory. During our joint research on uric acid, Wöhler one day sent me a crystalline body which he had obtained by the action of peroxide of lead upon this acid: I immediately thereupon wrote to him with great joy, and without having analysed the body, that it was allantoin. Seven years before I had had this body in my hands; it had been sent to me by C. Gmelin for investigation, and I had published an analysis of it in *Poggendorff's Annalen*; since that time I had not seen it again. But when we had analysed the substance obtained from uric acid there appeared a difference in the amount of carbon, the new body gave $\frac{1}{2}$ per cent carbon less, and since the nitrogen had been determined by the qualitative method a corresponding quantity (4 per cent) of nitrogen more; consequently it could not possibly be allantoin. However, I trusted my eye memory more than my analysis, and was quite sure that it was allantoin, and the thing now to be done was to find the remains of the substance previously analysed in order to analyse it afresh. I could describe the little glass in which it was with such precision that my assistant at last succeeded in picking it out from amongst a couple of thousand other preparations. It looked exactly like our new body, except that examination under the lens showed that Gmelin, in the preparation of his allantoin, had purified it with animal charcoal, some of which having passed

through the paper in the filtration had become mixed with the crystals.

Without the complete conviction which I had that the two bodies were identical, the allantoin produced artificially from uric acid would undoubtedly have been regarded as a new body, and would have been designated by a new name, and one of the most interesting relations of uric acid to one of the constituents of the urine of the foetus of the cow would perhaps have remained for a long time unobserved.

In this manner it came to pass that everything I saw remained intentionally or unintentionally fixed in my memory with equal photographic fidelity. At a neighbouring soap boiler's I saw the process of boiling soap, and learned what "curd soap" and "fitting" are, and how white soap is made; and I had no little pleasure when I succeeded in showing a piece of soap of my own making, perfumed with oil of turpentine. In the workshop of the tanner and dyer, the smith and brass founder, I was at home, and ready to do any head's turn.

In the market at Darmstadt I watched how a peripatetic dealer in odds and ends made fulminating silver for his pea-crackers. I observed the red vapours which were formed when he dissolved his silver, and that he added to it nitric acid, and then a liquid which smelt of brandy, and with which he cleaned dirty coat collars for the people.

With this bent of mind it is easy to understand that my position at school was very deplorable; I had no ear-memory and retained nothing or very little of what is learned through this sense; I found myself in the most uncomfortable position in which a boy could possibly be; languages and everything that is acquired by their means, that gains praise and honour in the school, were out of my reach; and when the venerable rector of the gymnasium (Zimmermann), on one occasion of his examination of my class, came to me and made a most cutting remonstrance with me for my want of diligence, how I was the plague of my teachers and the sorrow of my parents, and what did I think was to become of me, and when I answered him that I would be a chemist, the whole school and the good old man himself broke into an uncontrollable fit of laughter, for no one at the time had any idea that chemistry was a thing that could be studied.

Since the ordinary career of a gymnasium student was not open to me, my father took me to an apothecary at Heppenheim in the Hessian Bergstrasse; but at the end of ten months he was so tired of me that he sent me home again to my father. I wished to be a chemist, but not a druggist. The ten months sufficed to make me completely acquainted alike with the use and the manifold applications of the thousand and one different things which are found in a druggist's shop.

Left to myself in this way, without advice and direction, I completed my sixteenth year, and my persistent importunity at last induced my father to give me permission to go to the University of Bonn; whence I followed to Erlangen the Professor of Chemistry, Kastner, who had been called to the Bavarian University. There arose at that time at the newly-established University of Bonn an extraordinary quickening of scientific life; but the degenerate philosophical methods of investigation, as they had been embodied in Oken, and still worse in Wilbrand, had a most pernicious influence on the branches of natural science, for it had led alike in lecture and in study to a want of appreciation of experiment and of an unprejudiced observation of nature, which was ruinous to many talented young men.

From the professional chair the pupil received an abundance of ingenious contemplations; but, bodiless as they were, nothing could be made of them.

The lectures of Kastner, who was considered a most eminent chemist, were without order, illogical, and arranged just like the jumble of knowledge which I carried about in my head. The relations which he discovered

between phenomena were somewhat after the following pattern :—

"The influence of the moon upon the rain is clear, for as soon as the moon is visible the thunder-storm ceases," or "the influence of the sun's rays on water is shown by the rise of the water in the shafts of mines, some of which cannot be worked in the height of summer." That we see the moon when the thunderstorm is dispelled, and that the water rises in the mine when the brooks which drive the pumps dry up in summer, was, of course, too blunt an explanation for a clever lecture.

It was then a very wretched time for chemistry in Germany. At most of the universities there was no special chair for chemistry; it was generally handed over to the professor of medicine, who taught it, as much as he knew of it, and that was little enough, along with the branches of toxicology, pharmacology, materia medica, practical medicine, and pharmacy.

Many years after this in Giessen, descriptive and comparative anatomy, physiology, zoology, natural history, and botany were in one single hand.

While the labours of the great Swedish chemist, the English and French natural philosophers, Humphry Davy, Wollaston, Biot, Arago, Fresnel, Thenard, and Dulong opened up entirely new spheres of investigation, all these inestimable acquisitions found no soil in Germany where they could bear fruit. Long years of war had undermined the well-being of the people, and external political pressure had brought in its train the desolation of our universities, filled men with painful anxiety for many years, and turned their desires and their strength in other directions. The national spirit had asserted its freedom and independence in ideal spheres, and by the destruction of belief in authority had brought rich blessings in many ways—for example, in medicine and philosophy; only in physiology it had broken through its natural limits, and wandered far beyond experience.

The goal of science and the fact that it has value only when it is useful to life had almost dropped out of sight, and men amused themselves in an ideal world which had no connection with the real one. It was considered an almost debasing sentiment, and one unworthy of an educated person, to believe that in the body of a living being the crude and vulgar inorganic forces played any part. Life and all its manifestations and conditions were perfectly clear. Natural phenomena were clothed in bewitchingly lovely dress, cut out and fitted by clever men, and this was called philosophical investigation. Experimental instruction in chemistry was all but extinct at the universities, and only the highly-educated pharmacists, Klaproth, Hermbstädt, Valentin Rose, Trommsdorff, and Buchholz, had themselves preserved it, but in another department.

I remember at a much later period, Professor Wurzer, who held the chair of chemistry at Marburg, showing me a wooden table drawer, which had the property of producing quicksilver every three months. He possessed an apparatus which mainly consisted of a long clay pipe stem, with which he converted oxygen into nitrogen by making the porous pipe stem red hot in charcoal, and passing oxygen through it.

Chemical laboratories, in which instruction in chemical analysis was imparted, existed nowhere at that time. What passed by that name were more like kitchens filled with all sorts of furnaces and utensils for the carrying out of metallurgical or pharmaceutical processes. No one really understood how to teach it.

I afterwards followed Kastner to Erlangen, where he had promised to analyse some minerals with me; but unfortunately he did not himself know how to do it, and he never carried out a single analysis with me.

The benefit which I gained through intercourse with other students during my sojourn in Bonn and Erlangen was the discovery of my ignorance in very many subjects which they brought with them from school to the university, and since I got nothing to do in chemistry I laid out

all my energies to make up for my previously neglected school studies.

In Bonn and Erlangen small numbers of students joined with me in a chemico-physical union, in which every member in turn had to read a paper on the question of the day, which, of course, consisted merely in a report on the subjects of the essays which appeared monthly in *Gilbert and Schweigger's Journal*.

In Erlangen, Schelling's lectures attracted me for a time, but Schelling possessed no thorough knowledge in the province of natural science, and the dressing up of natural phenomena with analogies and in images, which was called exposition, did not suit me.

I returned to Darmstadt fully persuaded that I could not attain my ends in Germany.

The dissertations of Berzelius, that is to say, the better translation of his handbook, which had a large circulation at that time, were as springs in the desert.

Mitscherlich, H. Rose, Wöhler, and Magnus had then repaired to Berzelius, in Stockholm; but Paris offered me means of instruction in many other branches of natural science, as, for instance, physics, such as could be found united in no other place. I made up my mind to go to Paris. I was then seventeen and a half years old. My journey to Paris, the way and manner in which I came in contact with Thenard, Humboldt, Dulong, and with Gay-Lussac, and how the boy found favour in the sight of those men, borders on the fabulous, and would be out of place here. Since then it has frequently been my experience that marked talent awakens in all men, I believe I may say without exception, an irrepressible desire to bring about its development. Each helps in his own way, and all together as if they were acting in concert; but talent only compels success if it is united with a firm indomitable will. External hindrances to its development are in most cases very much less than those which lie in men themselves; for just as no one of the forces of nature, however mighty it may be, ever produces an effect by itself alone, but always only in conjunction with other forces, so a man can only make valuable that which he learns without trouble, or acquires readily, for which, as we say, he has a natural gift, if he learns many other things in addition, which perhaps cost him more trouble to acquire than other people.

Lessing says that talent really is *will and work*, and I am very much inclined to agree with him.

(To be continued).

THE SEPARATION OF TITANIUM, CHROMIUM, ALUMINUM, IRON, BARIUM, AND PHOSPHORIC ACID IN ROCK ANALYSIS.

By THOMAS M. CHATARD.

HAVING to examine some magnesian silicate rocks, containing, in addition to iron and aluminum, small quantities of titanium, chromium, barium, and phosphoric acid, the methods for the decomposition of such rocks and the separation of their constituents were studied and compared so as to determine the most advisable manner of procedure. After repeated trials the following course, combining a number of well-known methods, has been found to be the most satisfactory.

The silica and bases are determined by the ordinary sodium carbonate fusion method, in which the hydrates of titanium, chromium, iron, and aluminum, together with the phosphoric acid, are precipitated together, and, after weighing, fused with sodium bisulphate, dissolved, the small amount of silica separated, and the solution, after reduction of the ferric oxide, titrated for total iron.

To separate these oxides, and at the same time to determine the barium, 2 grms. of the finely pulverised mineral are put into a platinum crucible or dish, moistened with water, dilute sulphuric acid (1:1) and pure strong

hydrofluoric acid added in considerable excess, the vessel put on a radiator to evaporate, and stirred from time to time. When the solution is so far evaporated that fumes of sulphuric acid begin to come off, there should still be so much acid present as to form a solution or emulsion, and not a paste, since the paste is liable to bake on the bottom of the vessel and form the difficultly-soluble anhydrous sulphates produced by overheating, especially when magnesia is present in quantity. At this point it is well to add a few drops of nitric acid to oxidise the ferrous oxide, and a little more hydrofluoric acid to ensure the complete expulsion of the silica. The evaporation is then continued until the sulphuric acid fumes strongly and no odour of hydrofluoric acid can be detected when the solution is cooled below the point at which the sulphuric acid fumes.

About 25 c.c. of dilute hydrochloric acid (1:5) is now added, the stirring being continued, and the material is then evaporated on the water-bath until most of the hydrochloric acid has been driven off. The material is then washed into a beaker, and any residue adhering to the vessel can be removed by a few drops of hot, strong hydrochloric acid, the vessel being rubbed with a bit of paper if necessary. If the solution be very turbid it can be digested on the water-bath for some time, but ultimately it is diluted with hot water to 250–300 c.c., allowed to stand for several hours, and then filtered.

The residue contains the barium as sulphate, and sometimes the small amounts of chromite or other minerals of the same class. It is washed, ignited, and thoroughly fused with sodium carbonate in a small crucible, the fused mass being then digested with hot water and leached. The well-washed residue is dissolved on the filter with dilute hydrochloric acid, and this solution filtered through the same filter, which, after washing, is burned, the ash fused with a little sodium carbonate, the mass dissolved in dilute hydrochloric acid and added to the leachings, which are now acidified and added to the main solution, after reduction of the chromic acid. The hydrochloric acid solution containing the barium is evaporated to a few drops to get rid of the excess of acid, diluted, the barium precipitated, and the filtrate from the barium sulphate added to the main solution.

This main solution, which should be perfectly clear and contain the iron and chromium as sesquioxides, is now made alkaline by ammonia and the precipitate re-dissolved by dilute hydrochloric acid. A few drops of acetic acid are added, the liquid brought to a boil, ammonia added in very slight excess, the boiling continued for a few minutes, and the precipitate filtered and washed. As the sole reason for this precipitation is to get rid of the magnesia and the accumulation of other salts, the washing need not be thorough, but the filtrate must be tested and the precipitation proved complete.

The precipitate is dissolved in hot dilute hydrochloric acid. The filter, after washing, is burned in a large platinum crucible, into which the solution, concentrated to a small bulk, is put and evaporated on the water-bath till it becomes pasty. Just enough water is now added to dissolve the salts, and then dry sodium carbonate is added in small portions, with continual stirring, till a comparatively dry mass results. This must be carefully done, for if too much soda is added at a time, and each addition is not thoroughly stirred into the mass, the after fusion is apt to be "lumpy" and unsatisfactory.

When a good excess of carbonate has thus been added, the mass is dried and gradually brought to clear fusion, which should be continued for half an hour. If lumps form, which is, however, rarely the case if lime and magnesia are absent and the foregoing directions are followed, they can be broken up by shaking the crucible with a circular motion to detach them from its walls. When the fusion is complete the mass is spread around the walls of the crucible and slightly cooled. A small quantity of sodium nitrate is now added, the whole rapidly fused and carefully boiled for not more than five minutes; it is then

again spread over the crucible and rapidly cooled with a blast of air. The mass is boiled with water till completely disintegrated, and then leached: repeated tests have shown that the residue which contains the titanium is, when well washed, free from chromium and phosphoric acid.

The washed residue is dissolved in hot dilute hydrochloric acid, the filter burned, the ash fused with sodium bisulphate, dissolved in water, and added to the solution. The titanium in this solution is separated by the excellent method of Dr. Gooch,* all the details as laid down by him being followed. I have, however, found it convenient, after the destruction of the tartaric acid by potassium permanganate, and the clearing of the solution by sulphurous acid, to add ammonia in slight excess, then at once acetic acid in excess, and boil with addition of sulphurous acid. The precipitate of titanium hydrate, mixed with some alumina, is filtered and washed with water containing sulphurous acid and a little acetic acid. It is thus freed from manganese and brought into a small compass, rendering the after work easier. Before the final precipitation of the titanium, the platinum generally in the solution should be removed by hydrogen sulphide.

The filtrate containing the chromic and phosphoric acids is heated, and ammonium nitrate cautiously added till no further precipitation of alumina occurs. The precipitation of the aluminum phosphate seems to be complete, but some alumina always remains in solution. The precipitate is allowed to settle, the supernatant liquid decanted, and the precipitate washed with a solution of ammonium nitrate until the yellow tinge disappears; it is then dissolved in dilute nitric acid, and the phosphoric acid precipitated by molybdate solution.

The filtrate containing the chromic acid is acidified, boiled, neutralised with ammonia, and the chromium precipitated by freshly prepared ammoniac sulphide. The precipitate, after some washing, is dissolved in hot dilute nitric acid, and, after concentration, potassium chlorate is added, the solution boiled, and finally evaporated nearly to dryness to expel the excess of acid. It is then diluted with cold water, and a saturated solution of sodium bicarbonate added in small excess, separating the last traces of alumina. After standing about three hours, the alumina is filtered and washed with moderately dilute solution of the bicarbonate. The filtrate is acidified, and the chromic acid reduced and precipitated by ammonium sulphide in a platinum dish, filtered, washed, re-dissolved to get rid of traces of alkali, re-precipitated, and finally weighed as chromic oxide.

This method, due to Baubigny, for the separation of aluminum from chromium, is very good and convenient if the solution be free from iron and contain but little alumina. Careful tests have shown that if iron be present some of it always remains in solution, while if there be much alumina it is almost impossible to wash out all of the chromate from the bulky precipitate with the cold solution of bicarbonate which must be used. It must also be noted in this connection that a solution of iron and chromium prepared by the Baubigny method was made ammoniacal; and it was proved that, while all of the iron was precipitated, this precipitate, even after the most careful washing with hot water, contained chromium.

Although the number of details in this process may seem very great, experience has shown that none of them can safely be neglected for the purpose of shortening the work; if the whole process be carefully followed out the results are very satisfactory, as shown by the following tests on a typical magnesium rock:—

	Percentage Cr ₂ O ₃ .	TiO ₂ .	BaO.	P ₂ O ₅ .
No. 1.	0.270	0.46	0.040	0.375
No. 2.	0.285	0.39	0.060	0.385
No. 3.	0.317	0.46	0.055	—
No. 4.	0.280	—	—	—
Average	0.288	0.44	0.052	0.380

* *Proc. Am. Acad.*, xli., 435 seq. (*Bull.*, No. 27, U. S. G. S. p. 16 seq.).

The use of sodium nitrate for the fusions is not absolutely necessary, though one is more sure of complete oxidation if it be employed. In the analysis of chrome ores the best results have been obtained by fusing the finely-pulverised ore with sodium carbonate alone, but keeping it in clear fusion for an hour. The fused mass is treated like an ordinary silicate fusion, the silica after weighing being volatilised by hydrofluoric acid, and the residue, usually small, again fused with sodium carbonate, giving a clear solution in hydrochloric acid. — *American Chemical Journal*, vol. xiii., p. 106.

EXPERIMENTS ON THE PRECIPITATION OF ANTIMONY FROM SOLUTIONS OF THE TARTRATE OF ANTIMONY AND POTASSIUM.*

By J. H. LONG and H. E. SAUER.

In an investigation by one of us on the polarisation of solutions of potassium antimony tartrate it was observed, incidentally, that several interesting features are presented in its precipitation by other salts, notably by carbonates, phosphates, and acetates. We have made this precipitation the subject of a series of tests, the main results of which are here given.

The tartrate used for the investigation was purified by several crystallisations from the purest obtainable commercial product. An amount sufficient for all tests was prepared, powdered, and preserved in uneffloresced condition in several stoppered bottles until used.

Precipitation by Sodium Carbonate.

When an alkaline carbonate is added to a solution of potassium antimony tartrate, a precipitate is not always formed immediately. In fact, by working at a low temperature, and mixing the solutions slowly more than the total amount of carbonate necessary for complete precipitation may be added without producing even an opalescence. The polarisation phenomena of such a mixture show that a chemical change of some kind has, however, taken place. When allowed to stand mixtures prepared in this way gradually become turbid, but without the escape of CO₂, and in time a precipitate settles out. The appearance of the precipitate may be very much delayed by mixing the solutions with the least possible agitation and by keeping the mixture in a cool place.

By boiling, of course, precipitation takes place immediately, and the amount of antimony thrown down stands in relation to the amount of carbonate used.

This precipitate is referred to in the American edition of Fresenius' Qualitative Analysis as antimonious hydroxide, but the composition is not given. A precipitate having the composition Sb₂H₄O₅ has been analysed by Schaffner. This corresponds to Sb₂O₃·2H₂O, or—



containing 74.08 per cent of antimony. In our investigations we find that the precipitate dried at 100° has practically the composition Sb₂O₃·H₂O, containing 78.4 per cent of antimony. Slight variations in the amount of water were, however, observed, and these seemed to depend on the temperature and other conditions of precipitation rather than on the temperature of drying. The amount of antimony found was occasionally greater than called for by the formula with one molecule of water.

In the first series of experiments our tests were carried out in this general manner. 5 grms. of the tartrate was dissolved in 60–70 c.c. of water and cooled to 20° C. To this solution a weighed amount of sodium carbonate, dissolved in a small amount of water, was added, and the

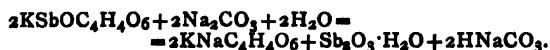
mixture diluted to exactly 100 c.c. at 20°. It was then allowed to stand 24 hours. Usually, in solutions containing only small amounts of carbonate, precipitation did not soon begin; in some solutions several hours elapsed, but in all cases as much precipitate as formed at all, settled out, leaving the supernatant liquid clear before the end of the 24 hours.

When abundant enough, a portion of the precipitate was taken for analysis, and the amount of antimony left in solution was also determined. This was done by conversion into sulphide, washing and drying with the usual precautions, and weighing in a Gooch filter. The analyses of the precipitates in this series gave, in the mean, 78.8 per cent of antimony. The general results of the experiments are given in this table.

No.	100 c.c. at 20°.			Percent of KSbOT. taken in solution.
	Amount of KSbOT. Grms.	Amount of Na ₂ CO ₃ . Grms.	Sb ₂ S ₃ from 50 c.c. Grms.	
1.	5	0.1	1.264	99.93
2.	5	0.3	1.078	85.22
3.	5	0.5	0.890	70.36
4.	5	0.7	0.718	56.76
5.	5	0.9	0.517	40.87
6.	5	1.2	0.369	29.17
7.	5	1.5	0.1763	13.94
8.	5	2.0	0.0493	3.88

It will be seen from a consideration of the numbers of the last column how incomplete is the precipitation even with an excess of the carbonate. For the precipitation of 5 grms. of tartrate, 0.7982 gm. of dry carbonate should be required on the assumption that 1 molecule of carbonate is sufficient for 2 of tartrate. But with these amounts, the table shows about one-half of the antimony is still in solution. We carried out numerous parallel tests, obtaining the same general results in all cases. Exactly the same values could not be expected of course, because the extent of precipitation seems to depend, not only on the amount of carbonate and the temperature, but on the manner of mixing the solutions, and whether they are much shaken or little. As explained above, we avoided agitation as far as possible in this series of tests.

The precipitation of antimony takes place here without the liberation of CO₂, and possibly according to this equation—



This equation is suggested by the behaviour of the solutions prepared by adding the carbonate, dissolved in a definite amount of water, from a burette to solutions of the tartrate containing 5 grms. in 100 c.c. The carbonate solutions had a strength of exactly 2 per cent, and when run into the tartrate solution containing a little phenolphthalein, as indicator, nearly 80 c.c. was required to give colour instead of 40, which would be sufficient for this equation—



From the behaviour on polarisation it is evident that a reaction takes place immediately on mixing the solutions. The amount of rotation is very much decreased, even without precipitation, from which it follows, apparently, that the antimony must exist in soluble form other than tartrate, as suggested by one of us elsewhere (*American Journal of Science*, October, 1890). Something will be said below as to the form in which the antimony may be held here.

A study of the last column in the table above shows that the antimony in solution diminishes very regularly as the amount of added carbonate is increased. The extent of precipitation at this temperature is much below

* From the *Journal of Analytical and Applied Chemistry*, v., No. 3.

what is called for by theory. The next tests were made with solutions mixed at the boiling heat.

The results are given in the following table:—

100 c.c. Mixed at 100° C.				
No.	Amount of K ₂ SO ₄ Grms.	Amount of Na ₂ CO ₃ Grm.	Sh ₂ S ₂ from 50 cc. Grm.	Per cent of K ₂ SO ₄ taken in solution.
9.	5	0.1	1.135	89.73
10.	5	0.5	0.608	48.06
11.	5	0.8	0.2608	20.61
12.	5	1.0	0.1618	12.80

Here the precipitation is much more complete than before. Something similar is shown in another series of tests where the solutions were mixed hot, the mixture being diluted to 100 c.c., and kept in boiling water one hour. The supernatant liquid was filtered off, and after cooling was diluted to 100 c.c.

In three cases mixtures were made as before, but diluted to 250 c.c. before heating one hour in the water-bath. The results are given below:—

100 c.c. Kept at 100° 1 Hour.				
No.	Amount of K ₂ SO ₄ Grms.	Amount of Na ₂ CO ₃ Grm.	Sh ₂ S ₂ in 50 c.c. Grm.	Per cent of K ₂ SO ₄ taken in solution.
13.	5	0.2	0.002	79.23
14.	5	0.5	0.5906	46.70
15.	5	0.8	0.2751	21.74
16.	5	1.1	0.1095	8.69
17.	5	1.5	0.0802	6.33
18.	5	2.0	0.0560	4.42
19.	5	3.5	0.0591	4.66
20.	5	5.0	0.0600	4.74

250 c.c. Kept at 100° 1 Hour.				
No.	Amount of K ₂ SO ₄ Grms.	Amount of Na ₂ CO ₃ Grm.	Sh ₂ S ₂ in 50 c.c. Grm.	Per cent of K ₂ SO ₄ taken in solution.
21.	5	0.2	0.423	83.60
22.	5	0.8	0.1170	23.12
23.	5	2.0	0.0342	6.76

It will be seen that the results of experiments 11, 15, and 22 are nearly the same, and also that the amount of antimony precipitated reaches a maximum to decrease in the solutions containing the largest amounts of sodium carbonate. The excess of this salt appears, therefore, to have a marked solvent action, increased by heat, as shown on comparing the results of experiments 18, 19, 20, and 23 with experiment 8. Precipitation seems to be least perfect in the dilute solutions as indicated by the last tests. No escape of CO₂ was observed here, while in the stronger solutions made and kept hot the loss was much less than we expected. We found 0.3445 grm. CO₂ in 25 c.c. of the filtrate from No. 19, equivalent to 94.9 per cent of the amount originally present, while in the filtrate of No. 20 we found 97.4 per cent of the total CO₂. In the strong solutions the conditions are naturally favourable for the retention of the gas.

We tried to secure more perfect precipitation in hot solutions than that shown in No. 18, but without much success. From considerations above, theoretically, precipitation should be completed by addition of 1.5964 grms. of the carbonate to the solution of 5 grms. of the tartrate, but a test made with these amounts showed as much antimony in solution as was left in No. 17, when only 1.5 grms. of the carbonate was taken. It is evident from polarisation phenomena that the antimony here present does not exist as tartrate, and the increased amount with increase of added soda suggests the gradual formation of antimonite, even before a maximum in the oxide is reached.

Complete precipitation, if possible at all, must be looked for only at very low temperatures, and a study of the connection between temperature, amount of soda, and precipitation would undoubtedly be an interesting one.

PROCEEDINGS OF SOCIETY

PHYSICAL SOCIETY.

May 22nd 1891.

Prof. W. E. AYRTON, F.R.S., President, in the chair.

Mr. F. H. NEVILLE was elected a member of the Society. Mr. C. J. WOODWARD exhibited Dr. Schobben's *Form of Lantern Stereoscopes*.

This instrument consists of a double lantern, by which the two pictures of a stereoscopic slide are projected on a screen. The two pictures are coloured complementary tints by placing pieces of red and green glass in front of the lenses, and each observer views the overlapping images through spectacles, the eyeglasses of which are also coloured red and green. The stereoscopic effect is very striking.

Mr. BOYS stated he had tried to obtain a similar result with the aid of polarised light, by viewing two polarised images through Nicol's prisms. No effect was obtained, owing to elliptic polarisation produced by the screen, but he thought that if a dead gold screen had been used instead of an ordinary one the effect might have been obtained.

Prof. PERRY, F.R.S., showed *A New Form of Steam Engine Indicator*.

A galvanometer mirror is fixed excentrically to a steel disc forming one side of a chamber communicating with the cylinder. The pressure of the steam bulges out the disc and causes the mirror to deflect a ray of light thrown on it in the ordinary way. A rotation at right-angles to the former is imparted by the movement of the piston rod. The ray of light traces out the diagram on a screen suitably placed, and the complete figure is continuously visible owing to the persistence of impressions. This indicator possesses advantages over other forms, in being free from errors due to friction, or oscillations of the springs and the alteration of their elasticity due to temperature changes. The errors of ordinary indicators are considerable at high speeds owing to the ripples introduced into the indicator diagram. If the natural period of the spring is one-twentieth of the time of a revolution, the diagram is fairly free from ripples, but if it is as much as one-tenth no amount of friction in the indicator will prevent ripples forming. In the new indicator, the natural period of the disc can be made very short.

The steel discs are easily removable, and can be proportioned to suit different pressures and speeds.

For experimental and teaching purposes it is advantageous to see at once the alterations in the diagram caused by changes of load, pressure, &c. Several diagrams were exhibited to the meeting.

In reply to Prof. CARUS WILSON, Prof. PERRY stated that the deflection was proportional to the pressure in the cylinder within the limits any particular disc was intended for.

Mr. ADDENBROKE thought the instrument an important improvement on its predecessors, and considered it would prove of great service to electrical engineers.

Mr. SWINBURNE said a peculiar merit of the indicator was that it could be permanently attached to an engine, like an ordinary pressure gauge. He suggested the use of a small telescope instead of the ray method.

The PRESIDENT thought that the instrument could be modified so as to be useful for analysing the shape of the curves representing alternating currents.

"On Blakesley's Method of Measuring Power in Transformers." By Prof. PERRY, F.R.S.

This paper refers to the supposed error in Mr. Blakesley's formula, due to the fact that transformers show magnetic leakage. The proofs of the formula hitherto given have been obtained by treating the equa-

CIET] In the manner first adopted by Dr. Hopkinson. On this system the reactions of the primary and secondary currents are represented by the equations—

$$V = R_1 C_1 + P \frac{dN}{dt} \quad 0 = R_2 C_2 + S \frac{dN}{dt};$$

where P and N are respectively the turns on the primary and secondary coils, and N is the magnetic flux between the coils. Here it is assumed that there is no magnetic leakage, and the author thinks that on this account the method is inferior to the original method of Maxwell, in which the induced electromotive forces are expressed in terms of coefficients of self and mutual induction. On the assumption that there are no eddy currents, Maxwell's equations are—

$$V = R_1 C_1 + L_1 \dot{C}_1 + M \dot{C}_2, \quad 0 = R_2 C_2 + M \dot{C}_1 + L_2 \dot{C}_2;$$

in which, although L_1 , M, and L_2 may not be constant, it may be assumed that they are respectively proportional to P, PS, and S if there is no magnetic leakage, and if the amount of magnetic leakage bears a constant proportion to the whole flux, the three quantities may still be assumed proportional to each other, although M^2 is less than $L_1 L_2$. From these equations we obtain—

$$VC = R_1 C_1^2 - R_2 \frac{M}{L_2} C_1 C_2 + \frac{L_1 L_2 - M^2}{L_2} C_2 \dot{C}_1.$$

Hopkinson puts down the last term as zero, but owing to the very rapid rate at which C_1 changes, the last term is very important, even though M may be but a small percentage less than $\sqrt{L_1 L_2}$. On integrating this equation, the first two terms on the right-hand side yield Blakesley's formula, and the last term vanishes in the integral, because, however great, the magnetic leakage may be—

$$\int C_1 \dot{C}_1 dt = 0$$

when taken over a period, because the functions are periodic.

Mr. Blakesley's formula thus appears to hold, whatever the magnetic leakage. The paper contains several tables of calculations showing the effect of magnetic leakage on the value of the terms in the equation.

Mr. BLAKESLEY said he doubted the correctness of the assumption that the value of M was the same in the two equations, and thought that the result arrived at must be incorrect.

Dr. SUMPNER did not doubt that if the coefficients could be considered constant, the formula was true whatever the leakage, but he did not consider that the action of transformers justified such an assumption. If the formula were true it would also hold if there were eddy currents, as these would merely produce the effect of additional secondary coils. He had analysed Blakesley's method by using a modification of the Hopkinson equations, and had shown that the power as estimated by Blakesley's formula had to be lessened by the fraction represented by the expression—

$$X = \frac{\int x A_p \int A_s dt dt}{E + \int A_p A_s dt}$$

where A_p and A_s are the instantaneous values of the primary and secondary currents, and x is such that $N_p = N_s(1+x)$, where N_p and N_s are the fluxes of magnetism through the primary and secondary coils at the same instant; E is a negligibly small quantity compared with the rest of the denominator. In obtaining this factor no assumption whatever had been made, and it was easy to see that if A_p and A_s could be assumed sine functions, and x a constant, the value of the factor X became x simply. In only one case did X reduce to zero, and that was when x was a sine function of the same period as A_p and A_s . He believed that in actual transformers x was approximately constant.

Mr. SWINBURNE pointed out that the split dynamometer was merely a wattmeter, and stated that he had transformers which, owing to magnetic leakage, would indicate an efficiency of over 100 per cent if tested by Blakesley's method. If this method gives an efficiency of 96 per cent, and leakage causes a drop of 2 per cent in E.M.F., the real efficiency is only about 94 per cent. He thought that the assumption that the currents followed a sine law was equivalent to supposing that there was no loss in hysteresis.

The PRESIDENT said that no one would be more glad than himself to find that Mr. Blakesley's method was accurate, but he could not agree with Prof. Perry that Dr. Hopkinson was wrong in abandoning the academical method of Maxwell.

Prof. PERRY replied to the various points raised in the discussion.

A paper on "Current and Potential Difference Analogies in the Methods of Measuring Power," by Prof. W. E. AYRTON and Dr. SUMPNER, was postponed.

NOTICES OF BOOKS.

The Romance of Science. Coal and What We Get from It. A Romance of Applied Science. Expounded from the Notes of a Lecture delivered in the Theatre of the London Institution, January 20th, 1890. By RAPHAEL MELDOLA, F.R.S., F.C.S., &c., Professor of Chemistry in the Finsbury Technical College, City, and Guilds of London Institute. Published under the direction of the Committee of General Literature and Education appointed by the Society for Promoting Christian Knowledge. London: Society for Promoting Christian Knowledge, Northumberland Avenue, W.C.

PROFESSOR MELDOLA's undertaking to give an intelligible account of the successive stages in the development of the coal-tar industry without assuming any knowledge of chemical science on the part of the reader is undeniably bold. At the same time we must pronounce it at once meritorious and signally successful. An account both popular and scientific of one of the most interesting and complicated branches of industrial chemistry has been hitherto a desideratum. The subject is, indeed, a somewhat hackneyed one in semi-scientific lectures and after dinner speeches, but its treatment is ordinarily superficial and even inaccurate. Some speeches even congratulate us that we have "no longer to ransack the hemispheres for colouring materials, but find them at our very feet." This is, indeed, a misapprehension, for although coal-tar is produced in Britain in greater quantity than in any other country, yet its elaboration into dye-ware is carried on only to a comparatively small extent in this, the birth-land of the industry in question. Hence the technology of coal-tar and its products is to every true Briton a "sore subject." We cannot help asking ourselves whether we shall ever succeed in wiping off this stigma and in assuming our legitimate place with respect to the colour manufacture. We must never forget that though pure science is absolutely cosmopolitan, yet applied science is more and more becoming a phase of war. Thus the invention of artificial alizarin has been a most disastrous event for certain districts in the south of France. Prof. Meldola justly says that the cultivation of the madder plant has had to be abandoned, and that the vast tracts of land devoted to this purpose have become available for other crops. But unfortunately there is no other crop suitable to the locality equally or more remunerative. Had such crops existed they would have been cultivated in preference to madder. But at present no little of the former madder-land is lying waste. Similar is the case with the cochineal, turmeric, safflower, &c., plantations. Should the attempts at the synthetic production of indigo prove commercially successful much British capital and

much of the finest land in India will be thrown out of use. Hence the triumphs of organic synthesis have their shadow-side. What is gained by one country or one manufacture is taken from another. Hence we cannot afford to stand by and watch the transformation which industrial chemistry is effecting. In self-defence we must keep our place in the front line. Such establishments as the City and Guilds of London Institute are as essential to our safety as are our cruisers and torpedoes. The only misfortune is that in obedience with the dictates of examinationism we have to expend both more money-power and more brain-power in obtaining equal results than have our rivals. There are few thoughtful men who will not, if they open Professor Meldola's book, read it both with pleasure and profit. The way in which seemingly distinct departments of practical chemistry are shown to be correlated will prove, indeed, a chapter in the "Romance of Science."

Fifteenth Annual Report of Her Majesty's Inspectors of Explosives: Being their Annual Report for the Year 1890. Presented to both Houses of Parliament by Command of Her Majesty. London: Her Majesty's Stationery Office.

THIS report is from several points of view highly satisfactory. The number of deaths from manufacturing accidents is but eight, being slightly below the average (8·1) of the past ten years. These figures are the more important as the number of factories, their output, and the number of hands employed are increasing. The vigilance of the inspectors is fairly maintained, and the local authorities are becoming more alive to their duty in this respect. Steps are being taken to check the illegal practice of storing explosives in miners' houses, which has been too prevalent in Northumberland. It will scarcely be believed that it has been found necessary to warn traders against delivering explosives to young children. At Broxbourne a child of seven was actually sent alone to fetch explosives from a store.

The year has not been marked by any of those occurrences which would formally have been denominated treasonable outrages, but which are now euphemistically called "private warfare." Nor have there been in the United Kingdom any of those sweeping calamities which have occurred in former years. The only cases which called for special inquiry have been the explosion at Roslin Gunpowder Factory, January 22nd, 1890; the nitro-glycerin explosion at Colwill Quarry, Devonshire, February 18th, 1890; the explosion of gunpowder and gun-cotton near Buxton, March 1st, 1890; the explosion of a magazine at Pain's Firework Factory, July 6th, 1890; and the explosion of the glazing-house at Roslin Gunpowder Factory, October 22nd, 1890.

The number of persons employed in these arts appears to be 9820 persons in the regular factories, plus 206 persons *known* (the italics are the inspectors) to be employed in "small" and "toy" firework factories, or, in all, 10,026.

The first Roslin accident, which involved the loss of six lives, was traced to the bringing of matches into the factory.

The second Roslin accident was due to the use by one of the deceased of a steel implement, in deliberate violation of the rules. The inspectors very rightly contend for the establishment of "a rigorous, even a semi-military discipline in factories of explosives."

The new explosive "ballistite" will have to be watched, and its risks guarded against.

Of the fifteen accidents in the manufacture of nitro-glycerin preparations, nine are referable to decompositions of the material.

Two more attempts have been made to render the chlorates practically available. Cycene No. 1 was condemned as becoming more sensitive to friction and per-

cussion on keeping. Cycene No. 2 stood the tests more successfully, but it was diluted with a nitrate and a large percentage of combustible matter.

It is pointed out that nitro-compounds like dinitrobenzole are scarcely if at all affected by traces of acid, and under such circumstances show no tendency to spontaneous decomposition.

On the other hand, such nitro-compounds as gun-cotton and nitro-glycerin (which are, more strictly speaking, nitric ethers) are seriously affected by traces of acids.

Not a few serious accidents have been due simply to recklessness in playing with explosives, fuses, and detonators. But equal recklessness is shown by people who let such articles remain in unsafe and improper places.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxii., No. 19, May 11, 1891.

On a New Oxide of Tungsten.—E. Péchard.—The author has previously announced (*Comptes Rendus*, vol. cxii., p. 720), that hydrogen peroxide converts alkaline paratungstates. It was interesting to examine if this reaction gave rise to the salts of a higher acid, *i.e.*, to pertungstates analogous to the permolybdates which the author has described. A solution of sodium paratungstate, mixed with hydrogen peroxide and boiled for a few minutes, quickly takes a yellow colour. No sodium paratungstate is then present. If the yellow liquid thus obtained is evaporated in a dry vacuum it deposits small, white, radiating crystals, which are distinguished from the paratungstate by their great solubility in water. These crystals ($\text{NaO}, 2\text{H}_2\text{O}, \text{W}_2\text{O}_7$), contain a per-acid, $\text{W}_2\text{O}_7\text{Aq}$.

Thermic Study of Bibasic Organic Acids having Simple Functions.—G. Massol.—This paper and the accompanying remarks by M. Berthelot do not admit of useful abstraction.

On the Fourth Primary Amylic Alcohol.—L. Tisserier.—The author has sought for the trimethylethyl-alcohol, $(\text{CH}_3)_3\text{C}-\text{CH}_2\text{OH}$, and is engaged with the further study of this alcohol and its derivatives.

Vol. cxii., No. 20, May 19, 1891.

At the opening of the Session the Académie was informed of the death of the illustrious physicist Edmond Becquerel, which took place on the 11th inst.

On the Combustion- and Formation-Heat of Organic Chlorides.—MM. Berthelot and Matignon.—This memoir does not admit of useful abstraction.

Quantitative Studies on the Chemical Action of Light. Part 3: *Influence of Dilution*.—Georges Lemoine.—Setting aside the effects of absorption the author concludes that the chemical actions set up by light and by heat follow the same laws.

Calculation of the Temperatures of Fusion and Ebullition of the Normal Paraffins.—G. Hinrichs.—The results are given in the form of tables.

The Influence of the Alkaline Bases upon the Solubility of the Alkaline Salts.—M. Engel.—One mol. of anhydrous potassa or soda, (M_2O), precipitates approximately 1 mol. of the alkaline salt. The action of ammonia upon ammoniacal salts is different from that of potassa and soda upon potassium and sodium salts. The presence of ammonia scarcely diminishes at the outset the solubility of ammonium chloride and afterwards increases it decidedly.

The Determination of Silica in Presence of Iron.—M. Leclerc.—The presence of a large quantity of iron is generally considered capable of interfering with the determination of silica by evaporation to dryness. The decomposition of ferric chloride may be avoided by uniting it with potassium chloride so as to form a double salt, which is well known, and which has been long ago utilised by M. Schloessing. For instance, in the determination of silicon in cast-iron, 1 gm. of the metal is treated with 20 c.c. of nitric acid and 10 c.c. of hydrochloric acid. After the reaction is over the chief part of the nitric acid is expelled at ebullition with two successive additions of hydrochloric acid—30 c.c. each; 3 grms. of ammonium chloride are added, and the liquid is concentrated to the state of a syrup. The evaporation is completed in the stove, so as to expel the last traces of the nitro compounds in the state of gas. The residue is taken up in hydrochloric acid; there are added 3 grms. pure potassium chloride and water enough to dissolve it, and the evaporation is then continued to dryness. The double iron and potassium salt crystallises at the same time as a certain quantity of double iron and ammonium chloride. These salts are soluble in cold water, but they are first dissolved in hydrochloric acid to remove accessory elements. The silica coagulates upon the residue of carbon; it filters and washes easily. After ignition at a high temperature it remains pulverulent, but dense and easy to weigh. Without the presence of ammonium chloride this silica would contain manganese; it would also be contaminated with potassa if all the nitric acid has not been previously expelled. Chrome is also redissolved completely by taking up the residue at first in concentrated acid. It is well to reduce a little of the chrome to chromous chloride by dissolving a little pure zinc or aluminium chloride in the liquid.

The Constitution and the Formation-Heat of the Bibasic Erythrates.—M. de Forcrand.—Not capable of useful abstraction.

On the Solution-Heat and the Solubility of some Organic Acids in Methyl, Ethyl, and Propyl Alcohols.—M. Timofeiew.—The author concludes that in the cases studied there is a correspondence between the molecular solubility and the heat of solution; the variation of the molecular solubility involving a variation of the heat of solution in the opposite direction.

Action of the Chlorides of the Bibasic Acids upon Sodic Cyanacetic Ether.—P. Th. Muller.—Not suitable for abridgment.

Formation of Nitrates in the Earth.—A. Müntz.—The rarity of nitrates in the soil, which seems to be in contradiction with the abundance of the nitrous ferments, depends on the rapid oxidation of the nitrates by the simultaneous action of carbonic acid and oxygen, which are always present in the atmosphere confined between the particles of the earth.

Archives Néerlandaises des Sciences Exactes et Naturelles.
Vol. xxiv., Parts 4 and 5.

On the Relations between Anhydrous Thorium Sulphate and its Hydrates, and on the Phenomena of Retardation in the Hydration and the Dehydration of this Salt.—H. W. Bakhuis Roozeboom.—The author's researches explain the apparent contradiction between the behaviour of anhydrous thorium sulphate and the general rules which he had given for the relations of the different hydrates of one and the same salt. In thorium sulphate hydration and dehydration are effected so slowly that there may result unstable conditions at great intervals of temperature.

On the Photogenic and Plastic Aliment of Luminous Bacteria.—W. Beyerinck.—This very interesting paper does not admit of useful abridgment.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. v., No. 6.

New Process for Oxidising Chrome Ores and Manufacturing Chromates.—J. Massignon and E. Vatel.—The yearly consumption of these salts in France alone averages two million kilos, yearly, representing a value of two million francs. There do not exist any chrome-works in France. The authors criticise the present method of manufacture, and examine the proposals made for its improvement, none of which they find satisfactory. They proceed as follows:—The ore, very finely ground, is mixed with calcium chloride and lime, or calcium carbonate, in such proportions that all the base derived from the caustic or carbonated lime introduced into the mixture may be a little in excess of what is required to convert all the chromium sesquioxide of the ore into calcium chromate, when this sesquioxide passes into the state of chromic acid. The calcium chloride is employed in the proportion of 1 equivalent to 3 of total lime. This mixture is obtained by working together the ground ore, and a paste is formed either with lime and calcium carbonate or calcium carbonate alone, slacked or stirred up in a strong solution of calcium chloride. If made with ground chalk it does not harden in the air; but if we use together lime and chalk the mixture sets like cement, and may be moulded into blocks or plates which become partially dry in the air. The air-dried blocks are placed in a furnace, where they are moderately heated to complete the desiccation, and then baked at a temperature sufficient to causticise the calcium carbonate. If the blocks are then left exposed to the air, at the common temperature, in about a month the oxidation is complete. The advantages of this process are economy of fuel and of labour; the waste of alkali is suppressed, and a larger proportion of the chromium oxide in the ore is utilised.

The Nitration of certain Aromatic Amines.—E. Noelling and L. Stocklin.—This memoir does not admit of useful abstraction.

Researches on the Colouring-matters derived from Triphenyl Methane.—E. Noelling.—The completion of a bulky memoir (Part 4) discussing the condensation-products of paranitrodimethylamidobenzhydrol with metatoluidin and its derivatives. Part 5 treats of the condensation-products of benzaldehyde and the nitrobenzaldehydes with the dialkylated derivatives of metatoluidin; and Part 6 deals with the condensation-products of orthoformic ether with dimethyl-metatoluidin and dimethyl-metaxylidin.

Vol. v., No. 7.

The Manufacture of Pure Yeast.—H. Elion.—This paper requires the two accompanying figures.

Action of Phosphorus Pentafluoride at a Red Heat upon Platinum Sponge.—Henri Moissan.—Platinum fluoride possesses the property of readily combining with the two gaseous phosphorus fluorides, producing a volatile crystalline compound, which is platinum fluorophosphide. It is also possible to form fluoroplatinum compounds by causing phosphorus pentafluoride to act upon very pure platinum sponge kept at a temperature a little above dark redness.

On the State of Bodies in Solution.—G. Wyrroboff.—The author concludes that salts may exist in solution in the state of hydrates.

On Homofluoresceine.—Edouard Grimaux.—On heating a mixture of orceine, chloroform, and soda, Herr Schwartz obtained a body, $C_{23}H_{18}O_5$, which he names trimethylfluoresceine or homofluoresceine. The author regards this body as identical with the orceine-aureine of Nencki, ($C_{22}H_{18}O_5$).

Formation of Coloured Lakes.—Léo Vignon.—The lakes obtained with stannic acid (safranine) were of a full red colour, whilst those obtained with metastannic acid were white, scarcely tinted with rose-colour.

MEETINGS FOR THE WEEK.

- TUESDAY, 9th.—Royal Institution, 3. "The Kemble Period of Stage History," by William Archer.
Royal Medical and Chirurgical, 8.30.
Photographic, 8.
WEDNESDAY, 10th.—Geological, 8.
THURSDAY, 11th.—Royal, 4.30.
Mathematical, 8.
Royal Institution, 3. "The Orchestra considered in connection with the Development of the Overture," by A. C. Mackenzie, Mus. Doc.
FRIDAY, 12th.—Royal Institution, 9. "The Rate of Explosion in Gases," by Prof. Harold Dixon, F.R.S.
Astronomical, 8.
Physical, 5. "Alternate Current and Potential Difference Analogies in the Methods of Measuring Power," by Prof. W. E. Ayrton, F.R.S., and Dr. W. E. Sumpner. "A Clock for Pointing out the Direction of the Earth's Orbital Motion in the Ether," by Prof. O. Lodge, F.R.S. "Some Experiments with Leyden Jars," by Prof. O. Lodge, F.R.S. "The Construction of Non-Inductive Resistances," by Prof. W. E. Ayrton, F.R.S., and Mr. Mather.
SATURDAY, 13th.—Royal Institution, 3. "The Scientific Study of Decorative Colour," by Prof. A. H. Church, M.A., F.R.S.

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President Elect—

WILLIAM HUGGINS, Esq., D.C.L., LL.D., F.R.S., F.R.A.S.

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THE CHEMICAL NEWS.

Vol. LXIII., No. 1646.

NOTE ON CINNAMIC ACID.

By Dr. T. L. PHIPSON, F.C.S., &c.

A REACTION by which cinnamic acid can be readily distinguished from benzoic acid and other compounds which resemble it more or less in appearance and properties, is the production of essence of almonds when dry cinnamic acid is treated with sulphuric acid and bichromate of potash. I find that when a small quantity of acid is kept for a few days in contact with sulphuric acid and bichromate of potash, without heating, the odour of hawthorn flowers thus produced gradually changes into an intense odour of honey. What produces the latter is yet unknown.

On various occasions, for some years past, I have endeavoured to produce cinnamic acid from the leaves of the bay (*Laurus nobilis*), but with only partial success. The long-continued frost of last winter killed the leaves and some of the branches of a fine bay tree in the garden of my villa at Putney, and these dead leaves contain a good deal of essence of cinnamon as compared with the fresh leaf.

It has been lately asserted that cinnamic acid is a more powerful antiseptic than salicylic acid; but this needs confirmation. It is said to destroy the virus (bacillus) of pulmonary tuberculosis.

Still more recently a spray of essence of cinnamon has been found more effective in the treatment of all forms of malarial fever than the usual treatment by quinine and arsenic. At Marguelane, in Turkestan, the spraying is performed several times daily in the hospital wards, and is stated to have proved more efficacious than essence of *Eucalyptus* used in the same manner.

DETERMINATION OF TURPENTINE IN PAINTS AND VARNISHES.

By H. JOSHUA PHILLIPS, F.I.C., F.C.S.

WHILE much information has been published with regard to the composition and fabrication of various paints and varnishes, there appears to have been very little done in the way of detailing methods of their analysis. The cause of this may be put down to the complicated nature of these substances, together with the many little difficulties that attend the proximate estimation of their constituents. In a recent analysis of a sample of an enamel the writer found the distillation method here described to answer well for the determination of turpentine, leaving the residuum of linseed oil, gum, and pigment in a fit state for further examination.

When paints or varnishes are distilled in air, it is known that oxidation-products are formed giving a low result for turpentine, while the residue of linseed oil, &c., is rendered useless for further examination owing to the formation of the inert linoxyn, &c. In ordinary cases the distillation may be conveniently carried on in a gentle current of coal-gas.

Fig. 1 is a sketch of the apparatus used by the writer. *B* is a three-way tube fitted into tubulure of the retort, *A*, through a cork, the end of the tube being about half an inch from the surface of the sample; into the part *B* a thermometer, *E*, is fitted, supported by a rubber plug at *C*. *D* is connected with a supply of coal-gas. *F* is a tared receiver, which is to be kept in a basin containing

cold water. *G* is a small tube for allowing the gas to escape. About 150 grms. of the sample are weighed into the retort, and connected to the tared receiver as in sketch. The retort is now suspended in a glass air-bath (a beaker with its bottom cut out is convenient), over wire-gauze on a tripod stand. Before proceeding with the distillation a gentle current of coal-gas is made to pass through the apparatus, and, when all the air has been driven out, the issuing gas is lighted at *G*, and the gas turned down until the flame is about the size of a

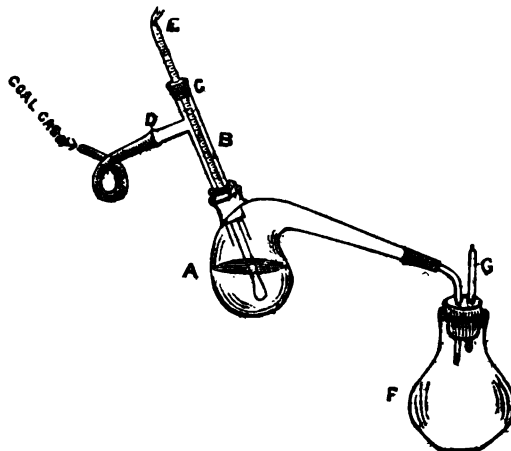


FIG. 1.

pea. A rush of gas must be avoided, or there would be a loss of turps. A small flame is now placed under the retort, and the distillation proceeded with gently. The turpentine should drop into the receiver without affecting the gas issuing at *G*. The temperature necessary for the complete expulsion of turps may be about 220° C. When all the turpentine has come over detach *F*, and plug the end of the retort with a cork, leaving the gas still turned on until it be required to examine the residuum, which is thus kept free from oxidation.

G. E. Railway Laboratory, Stratford, London, E.

A NEW METHOD OF MANUFACTURING SODA CRYSTALS, BASED ON PRACTICAL EXPERIENCE.

By THORVALD SCHMIDT.

IN the year 1886 a small factory in Copenhagen commenced the manufacture of soda in small crystals, $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$, i.e., in the same combination as ordinary soda crystals. The object was to supply the consumers of perfectly pure soda with the article required, without compelling them to spend time and money on crystallising the soda in order to obtain a pure article from the soda as usually sold.

By degrees, as this pure article became better known, customers began to ask for it at their grocers, and the result was an extension of the factory's working. Then came the Scandinavian Industrial Exhibition of 1888, at which this process was awarded a prize and attracted public attention in a still greater degree. Steady development of the work and increased familiarity with it caused further observations to be made with regard to the cooling process, which were turned to good use. On Messrs. Sthyr and Kjaer, of Copenhagen, buying the inventor's process, and supplying the necessary capital, improvements followed rapidly, till—at the end of 1890—a considerable enlargement of the factory was made, and the most perfect

apparatus supplied that many years' practical experience could suggest. The buildings, including alkali apparatus, weighing room, &c., occupy an area of about 160 square yards, and can produce about 20 tons daily, summer and winter, with a minimum result of 70 per cent $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$ of the contents of the lye. The temperature of the water used for cooling is not, however, unimportant, as the following examples, taken from the actual workings, will show:—

On the 10th December, 1890, the water was turned on at 10.30 a.m., and its temperature was 3 deg. Celsius (37.4 F.). At 2.30 p.m. the water was turned off, and the apparatus emptied. The crystallising process thus lasted four hours, and the result was 8 tons $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$.

On the 16th January, 1891, the process lasted from 10.30 a.m. to 2.30 p.m. The temperature of the water was again 3 deg. Celsius (37.4 F.), and the result was exactly the same as on the previous occasion.

On the 22nd May, 1891, the process lasted from 6.30 a.m. till 3 p.m., or 8½ hours, but the temperature of the water at the commencement was 13 deg. Celsius (55.4 F.). The result was again the same. These figures show clearly how very important it is to lower the temperature sufficiently, no less than 4½ hours having been saved by so doing.

In this factory there are three apparatus, and when the lye has been filled into them no attention is required, except that a look-out must be kept when they are ready, as the soda then runs down of its own accord on the drying apparatus.

The lye made in the evening is clear by next morning, and, with sufficiently cold water, can be ready by 10.30 a.m. if the filling is done by 6 a.m. By 12 noon the apparatus is again ready to take in new lye, and can be emptied again at 6 p.m., so that the soda crystals can, under favourable circumstances, be set four times daily—that is, with three apparatus 32 tons are produced every 24 hours; but in unfavourable circumstances, with water of a temperature of 13 degrees Celsius (55.4 F.), only twice, producing 16 tons. The soda is ready for weighing and delivery ten hours after being put on the drying apparatus. The whole process, from the lye to the finished soda, consequently only takes 36 hours at the outside. One man can fill the lye into three apparatus in three hours, or into ten apparatus daily. The only labour required is for the weighing and transporting of the finished soda, otherwise the apparatus does all the work itself with 4½ to 5 horse-power. The soda is filled into bags, partly because these are cheaper and partly because the soda is easier to handle in this form. Compared with the ordinary soda crystals, these crystals are just as durable, and will not become disintegrated in the bags. As the public are gradually getting accustomed to this new form of soda, the sale is increasing more and more, whilst they are discarding the kind formerly used, viz., the large crystals. The soda in small crystals is more convenient for weighing at the shop, it is easier to use in the household, and it is more economical for the consumer.

The new soda has had a marked influence on the exports of soda crystals from England to Denmark, which has fallen off considerably during the last few years.

If soda prepared according to Leblanc's method is used, the mother-liquid, alkali, must be treated in the ordinary way; whilst if soda by the ammonia process is used, the work can be done without interruption, the mother-liquid being used afresh. This method has been introduced into Germany, and several manufactories based on it are in course of construction there. Although doubtless it is a simple matter to dissolve calcined soda, whether done in Leblanc's or the ammonia process, every attempt at imitation has hitherto failed on account of the result being too insignificant in proportion to the labour involved,—besides which, if the apparatus are not handled with extreme care and accuracy, they fail to work properly.

In the factory belonging to Messrs. Sthyr and Kjaer the apparatus have been in constant use since last autumn, and not the slightest stoppage or accident has taken place. For this reason several German factories have had their apparatus made at Copenhagen of the best English steel, as they can thus be made under the inventor's personal supervision. An apparatus costs from £60 to £70, and always keeps clean.

Messrs. F. and A. Delcomyn have kindly undertaken to give all further information that may be required, and have also promised to carry out negotiations with intending buyers.

Copenhagen, May 23, 1891.

JUSTUS VON LIEBIG: AN AUTOBIOGRAPHICAL SKETCH.*

(Concluded from p. 267).

THE lectures of Gay-Lussac, Thenard, Dulong, &c., in the Sorbonne, had for me an indescribable charm; the introduction of astronomical or mathematical method into chemistry, which changes every problem when possible into an equation, and assumes in every uniform sequence of two phenomena a quite certain connection of cause and effect, which, after it has been searched for and discovered, is called "explanation" or "theory," had led the French chemists and physicists to their great discoveries. This kind of "theory" or "explanation" was as good as unknown in Germany, for by these expressions was understood not something "experienced," but always something which man must add on and which he fabricates.

French exposition has, through the genius of the language, a logical clearness in the treatment of scientific subjects very difficult of attainment in other languages, whereby Thenard and Gay-Lussac acquired a mastery in experimental demonstration. The lecture consisted of a judiciously arranged succession of phenomena, that is to say, of experiments whose connection was completed by oral explanations. The experiments were a real delight to me, for they spoke to me in a language I understood, and they united with the lecture in giving definite connection to the mass of shapeless facts which lay mixed up in my head without order or arrangement. The Antiphlogistic or French chemistry had, it is true, brought the history of chemistry before Lavoisier to the guillotine; but one observed that the knife only fell on the shadow, and I was much more familiar with the phlogistic writings of Cavendish, Watt, Priestley, Kirwan, Black, Scheele, and Bergmann, than with the antiphlogistic; and what was represented in the Paris lectures as new and original facts appeared to me to be in the closest relation to previous facts, so much so, indeed, that when the latter were imagined away the others could not be.

I recognised, or more correctly perhaps the consciousness dawned upon me, that a connection in accordance with fixed laws exists not only between two or three, but between all chemical phenomena in the mineral, vegetable, and animal kingdoms; that no one stands alone, but each being always linked with another, and this again with another, and so on, all are connected with each other, and that the genesis and disappearance of things is an undulatory motion in an orbit.

What impressed me most in the French lectures was their intrinsic truth, and the careful avoidance of all pretence in the explanations; it was the most complete contrast to the German lectures, in which the whole scientific teaching had lost its solid construction through the preponderance of the deductive method.

* Read at a joint Meeting of Societies in the Chemical Laboratories, University College, Liverpool, on Wednesday evening, March 18, 1891, by Prof. J. Campbell Brown, D.Sc.

An accidental occurrence drew A. von Humboldt's attention to me in Paris, and the interest which he took in me induced Gay-Lussac to complete in conjunction with me a piece of work which I had begun.

In this manner I had the good fortune to enjoy the closest intercourse with the great natural philosopher; he worked with me as he had formerly worked with Thenard; and I can well say that the foundation of all my later work and of my whole course was laid in his laboratory in the arsenal.

I returned to Germany, where through the school of Berzelius, H. Rose, Mitscherlich, Magnus, and Wöhler, a great revolution in inorganic chemistry had already commenced. Through the support of von Humboldt's warm recommendation, an extraordinary professorship of chemistry at Giessen was conferred upon me in my 21st year.

My career in Giessen commenced in May, 1824. I always recall with pleasure the twenty-eight years which I spent there; it was as if Providence had led me to the little university. At a larger university or in a larger place my energies would have been divided and dissipated, and it would have been much more difficult, and perhaps impossible, to reach the goal at which I aimed; but at Giessen everything was concentrated in work, and in this I took passionate pleasure.

The need for an institution in which the students could be instructed in the art of chemistry, by which I mean familiarity with chemical analytical operations, and skill in the use of apparatus, was then being felt; and hence it happened that on the opening of my laboratory for teaching analytical chemistry and the methods of chemical research, students by degrees streamed to it from all sides. As the numbers increased I had the greatest difficulty with the practical teaching itself. In order to teach a large number at one time it was necessary to have a systematic plan, or step by step method, which had first to be thought out and put to the proof.

The manuals which several of my pupils have published later (Fresenius and Will) contain essentially, with little deviation, the course which was followed at Giessen; it is now familiar in almost every laboratory.

The production of chemical preparations was an object to which I paid very particular attention; it is very much more important than is usually believed, and one can more frequently find men who can make very good analyses than such as are in a position to produce a pure preparation in the most judicious way. The formation of a preparation is an art, and at the same time a qualitative analysis, and there is no other way of making one's self acquainted with the various chemical properties of a body than by first producing it out of the raw material, and then converting it into its numerous compounds and so becoming acquainted with them.

By ordinary analysis one does not learn by experience what an important means of separation crystallisation is in skilful hands; and just as little the value of an acquaintance with the peculiarities of different solvents. Consider only an extract of a plant or of flesh which contains half a dozen crystalline bodies in very small quantities imbedded in extraneous matter, which almost entirely masks the properties of the others; and yet, in this magma, we can recognise by means of chemical reactions the peculiarities of every single body in the mixed mass, and learn to distinguish what is a product of decomposition and what is not, in order to be able to separate them afterwards by means which will exert no decomposing influence. An example of the great difficulty of finding the right way in such researches is afforded by the analysis of bile by Berzelius. Of all the numerous substances which he has described as its constituents no one is, properly speaking, contained in the natural bile.

An extremely short time had been sufficient for the famous pupils of the Swedish master to give a wonderful degree of perfection to mineral analysis which depends on an accurate knowledge of the properties of inorganic

bodies; their compounds and their behaviour to each other were studied in all directions by the Swedish school with a keenness quite unusual previously and even now unsurpassed. Physical chemistry, which investigates the uniform relations between physical properties and chemical composition, had already gained a firm foundation by the discoveries of Gay-Lussac and von Humboldt on the combining proportions of bodies in the gaseous state, and those of Mitscherlich on the relations between crystalline form and chemical composition; and in chemical proportions the structure appeared to have received its coping-stones and to stand forth completed. All that foreign countries had acquired in bye-gone times in the way of discoveries now yielded rich fruit also in Germany.

Organic chemistry—or what is now called organic chemistry—had then no existence. It is true that Thenard and Gay-Lussac, Berzelius, Prout, and Döbereiner, had already laid the foundations of organic analysis, but even the great investigations of Chevreul upon the fatty bodies excited but little attention for many years. Inorganic chemistry demanded too much attention, and, in fact, monopolised the best energies.

The bent which I acquired in Paris was in a quite different direction. Through the work which Gay-Lussac had done with me upon fulminating silver I was familiar with organic analysis, and I very soon saw that all progress in organic chemistry depended essentially upon its simplification; for in this branch of chemistry one has to do not with different elements which can be recognised by their peculiar properties, but always with the same elements whose relative proportions and arrangement determine the properties of organic compounds.

In organic chemistry an analysis is necessary to do that for which a reaction suffices in inorganic chemistry.

The first years of my career in Giessen I devoted almost exclusively to the improvement of the methods of organic analysis, and the immediate result was that there began at this little university an activity which had never before been seen.

For the solution of innumerable questions connected with plants and animals, on their constituents, and on the reactions accompanying their transformation in the organism, a kindly fate brought together the most talented young men from all the countries of Europe, and anyone can imagine what an abundance of facts and experiences I gained from so many thousands of experiments and analyses, which were carried out every year, and for so many years, by twenty and more indefatigable and skilled young chemists.

Actual teaching in the laboratory, of which practised assistants took charge, was only for the beginners; the progress of my special students depended on themselves. I gave the task and supervised the carrying out of it; as the radii of a circle have all their common centre. There was no actual instruction; I received from each individual every morning a report upon what he had done on the previous day, as well as his views on what he was engaged upon. I approved or made my criticisms. Every one was obliged to follow his own course. In the association and constant intercourse with each other, and by each participating in the work of all, everyone learned from the others. Twice a week, in winter, I gave a sort of review of the most important questions of the day; it was mainly a report on my own and their work combined with the researches of other chemists.

We worked from break of day till nightfall. Dissipations and amusements were not to be had at Giessen. The only complaint, which was continually repeated, was that of the attendant (Aubel), who could not get the workers out of the laboratory in the evening, when he wanted to clean it.

The remembrance of this sojourn at Giessen awakened in most of my pupils, as I have frequently heard, an agreeable sense of satisfaction for well-spent time.

I had the great good fortune, from the commencement of my career at Giessen, to gain a friend of similar tastes

and similar aims, with whom, after so many years, I am still knit in the bonds of warmest affection.

While in me the predominating inclination was to seek out the points of resemblance in the behaviour of bodies or their compounds, he possessed an unparalleled faculty of perceiving their differences. A keenness of observation was combined in him with an artistic dexterity, and an ingeniousness in discovering new means and methods of research or analysis such as few men possess.

The achievement of our joint work upon uric acid and oil of bitter almonds has frequently been praised; it was his work. I cannot sufficiently highly estimate the advantage which the association with Wöhler brought to me in the attainment of my own as well as our mutual aims, for by that association were united the peculiarities of two schools—the good that was in each became effective by co-operation. Without envy and without jealousy, hand in hand, we pursued our way; when the one needed help, the other was ready. Some idea of this relationship will be obtained if I mention that many of our smaller pieces of work which bear our joint names were done by one alone; they were charming little gifts which one presented to the other.

After sixteen years of the most laborious activity I collected the results gained, so far as they related to plants and animals, in my "Chemistry Applied to Agriculture and Physiology," two years later in my "Animal Chemistry," and the researches made in other directions in my "Chemical Letters." The last-mentioned was generally received as a popular work, which, to those who study it more closely, it really is not, or was not at the time when it appeared.

Mistakes were made, not in the facts, but in the deductions about organic reactions; we were the first pioneers in unknown regions, and the difficulties in the way of keeping on the right path were sometimes insuperable.

Now, when the paths of research are beaten roads, it is a much easier matter; but all the wonderful discoveries which recent times have brought forth were then our own dreams, whose realisation we surely and without doubt anticipated.

Here the manuscript ends, and it is to be hoped that more of it will yet be found.

Liebig's reference to Wöhler is very touching, and shows a side of his character which all his pupils knew well; they tell many genial stories illustrating his unselfishness and kindness of heart. One could have wished that he had not considered the stories "bordering on the fabulous," of how he "found favour in the sight of Humboldt, Gay-Lussac, and Thenard, out of place here." They would have been far from out of place. Mr. Muspratt supplies one of these stories as he heard it from Liebig's own lips, in the Munich Laboratory, as follows:—

Liebig frequently spoke, in most grateful terms, of the kind manner in which he—a youth barely eighteen—was received by Gay-Lussac, Thenard, and other eminent chemists, in Paris.

In the summer of 1823 he gave an account of his analysis of fulminating silver before the Academy. Having finished his paper, as he was packing up his preparations, a gentleman came up to him and questioned him as to his studies and future plans, and, after a most exacting examination, ended by asking him to dinner on the following Sunday. Liebig accepted the invitation, but, through nervousness and confusion, forgot to ask the name and address of his interviewer. Sunday came, and poor Liebig was in despair at not being able to keep his engagement.

The next day a friend came to him, and said—"What on earth did you mean by not coming to dine with von Humboldt yesterday, who had invited Gay-Lussac and other chemists to meet you?" "I was thunderstruck," said Liebig, "and rushed off, as fast as I could run, to von Humboldt's lodgings, and made the best excuses I could." The great traveller, satisfied with the explanation, told him it was unfortunate, as he had several members of the Academy at his house to meet him, but

thought he could make it all right if he would come to dinner next Sunday. He went, and there made the acquaintance of Gay-Lussac, who was so struck with the genius and enthusiasm of the youth that he took him into his private laboratory, and continued, in conjunction with him, the investigation of the fulminating compounds.

REACTIONS OF DIMETHYLMETAPHENETIDINE.

By EDOUARD GRIMAUX.

If carbonyl chloride is allowed to react upon this base in presence of aluminium chloride there is formed a fine blue colouring-matter, whilst under the same conditions dimethylaniline yields a crystalline violet. If purified by ordinary methods this compound has a great tinctorial power; it dyes a very pure and fine blue on silk, wool, and on cotton mordanted with tannin.

If the blue is heated with sulphuric acid to 100° it is destroyed and converted into a red fluorescent matter of feeble lustre, resembling the colour obtained by heating dimethylmetamidophenol with dehydrating-agents.

This blue must be regarded as a hexamethylated and trioxethylated derivative of rosaniline.

The meta-base yields a nitroso-derivative, which in most of its reactions behaves like nitroso-dimethylaniline. It yields oxazines with gallic acid, gallic ether, pyrogallol, resorcin, &c., eurrhodines with metadiamines, and an indophenol with α -naphthol.

Among the numerous colours thus obtained that furnished by resorcin is most remarkable for its beauty. If we heat a solution of resorcin and of the hydrochlorate of the meta-nitroso base, there is formed besides a non-fluorescent blue a colouring-matter which dyes silk of a fine violet, having a magnificent red fluorescence. Orcine and lutorcine behave like resorcin, but these fluorescent violets are not stable if exposed to light.

The nitroso-derivative of the meta-base differs from nitroso-dimethylaniline, as it does not yield with β -naphthol a blue analogous to Meldola's blue.

The meta-base has been submitted to various reagents with the following results:—

1. With phthalic anhydride alone no reaction; in presence of zinc chloride or sulphuric acid, formation of a red fluorescent colour, which appears identical with rhodamine.
2. With arsenic acid at 175°, a rose-colour, which does not appear to be an oxidation product, but results from the formation and condensation of dimethylamidophenol.
3. With phthalyl chlorides production of a green matter resembling the phthalic green derivative of dimethylaniline.
4. If heated with the chloride of dimethylmeta-amido-benzoic acid it gives a fine blue colouring-matter.
5. It turns rose-colour if heated with chloroform and soda.
6. If gently heated with phenylsulphonic chloride there is a violent reaction, with the transient formation of a blue matter quickly passing to a yellow.
7. With benzylic aldehyd and zinc chloride, with phenylchloroform, colouring-matters are also formed.

The ortho-base behaves quite differently from the meta base. It gives no colouring-matter with carbon oxychloride, phthalic anhydride, chloroform and soda, benzylic aldehyd or phenylchloroform.

The ortho-base with arsenic acid at 175°, or with phenylsulphurous chloride, gives a fine blue colour, which is also produced if the hydrochlorate is heated alone to 175°—180°.

Neither the meta- nor the ortho-base gives colours with copper chloride, which so readily converts dimethylaniline into Paris violet.

The author, in concert with M. Lefevre, has begun the study of the nitro-derivatives of the ortho- and meta-bases.—*Bulletin de la Soc. Chimique de Paris* (Series 3, vol. v., p. 647).

HYDRATED LEAD OXIDE.

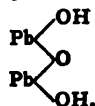
By C. LUEDEKING.

THERE seem to be at least two hydrated oxides of lead— $3\text{PbO}\cdot\text{H}_2\text{O}$ obtained by Payen (*Ann. Chim. Phys.* [4], viii., 302), and $2\text{PbO}\cdot\text{H}_2\text{O}$ prepared by Schaffner (*Ann. Chem.*, Liebig, li., 175). Payen obtained his hydrate in the form of strongly-refracting octahedra by allowing an ammoniacal solution of lead acetate to crystallise in a closed vessel. It is very questionable whether the crystals so obtained are entirely free from basic salt or ammonia. Calvert (*Compt. Rend.*, xxii., 480) observed that hydrated oxide of lead can combine with ammonia, and Winkelblech (*Ann. Chem.*, Liebig, xxi., 29) maintains that the hydrated oxide so obtained always contains small amounts of basic salt which cannot be removed by excess of alkali.

Schaffner claims to be able to obtain his hydrated oxide entirely free from basic salt by precipitating a solution of lead acetate with a slight excess of potassium hydrate.

It is possible to obtain the hydrated oxide of lead of Schaffner in excellent crystals in another way, which may form the basis for obtaining from other metals also hydrated oxides soluble in potassium hydrate. When litharge is boiled with a strong solution of potassium hydrate for some time, a considerable amount of it passes into solution. The potassium hydrate solution, when strong, deposits on cooling a large quantity of crystals of anhydrous protoxide of lead, as had been observed by several authors previously. The solution, after it has become perfectly cold, however, still contains a large amount of lead oxide. When now it is exposed in a small beaker to the air, carbon dioxide is slowly absorbed and potassium carbonate formed. Thus the lead is gradually and very slowly deprived of its solvent, and all conditions for crystallisation pertain. After several weeks the bottom of the vessel will be found covered with magnificently developed crystals, perfectly colourless and transparent, and having a high refractive power for light and brilliant lustre. These crystals, on examination, are found to be the hydrate, $2\text{PbO}\cdot\text{H}_2\text{O}$, in a state of absolute purity. They belong to the tetragonal system, are simple in development and short and thick in habit, showing the prism $\infty\text{P}\infty$, and the pyramid P at either end. The angle between the opposite edges, over the solid angle of the pyramid, is 101° . The axial relations are $1:1:0.824$. Their reaction is alkaline, and on exposure to the air they soon become opaque, absorbing carbon dioxide and forming lead carbonate. In this metamorphosis, however, they maintain sharply their original form. On heating they lose their water and become yellow litharge, but nevertheless maintain the original crystalline form.

The structure of this hydrate is, probably the following—



We may consider that it is rather to be expected that the weaker the base the fewer OH radicals will it contain. Take, for example, calcium hydrate—a much stronger base—and we have all the affinities of calcium saturated with hydroxyl groups.

The less the basic powers of an element, when it can form hydrates, the greater the likelihood of its forming

such hydrates as that we have examined, and even other such as $3\text{PbO}\cdot\text{H}_2\text{O}$, which has, in fact, been actually obtained. Thus it will be easy to form from a strong base a hydrated oxide containing the normal number of hydroxyl groups, while for a weak base this will be difficult, and *vice versa*. This will explain in a chemical way what appears at first anomalous and only mechanical admixture, viz., the small amount of water contained in many oxides of the heavier metals.—*American Chemical Journal*, vol. xiii., p. 120.

Chemical Laboratory, Washington University.

THE DISSOCIATION OF MAGNESIUM OXIDE BY MEANS OF METALLIC MAGNESIUM.

By H. N. MORSE and J. WHITE, Jun.

IN former papers (*Amer. Chem. Journ.*, xi., 258 and 348) we have described the dissociation which takes place when the oxides or sulphides of zinc and cadmium are heated in a vacuum with their respective metals. Since then we have found that the oxide of magnesium undergoes an equally unmistakable dissociation when it is heated in the same way with metallic magnesium.

The apparatus which we employed was essentially the same as that used in the dissociation of the oxides and sulphides of zinc and cadmium, except that, owing to the energetic action of the vapours of magnesium on silicates, it was found advantageous to enclose the mixture of oxide and metal in a tube of sheet-iron. The iron tube was made by forming a thoroughly-cleaned strip of the metal, from 40 to 45 centimetres long, around an iron rod of proper thickness, and closing one end with the hammer. It was then prepared for use by inclosing it in a glass tube, exhausting with the Sprengel pump, and heating to redness until it ceased to give off volatile matter.

Owing to the presence of considerable quantities of occluded hydrogen in commercial magnesium, as observed by Dumas (*Compt. Rend.*, xc., 1027), the metal was distilled in a vacuum in the manner described by Burton and Vorce (*Amer. Chem. Journ.*, xii., 219). The oxide of magnesium, also, was heated to redness in a vacuum until it ceased to give off carbon dioxide. The metal and then the oxide were dropped into the iron tube. This was then placed in a larger tube of hard glass which had been closed at one end. The length of the glass tube was usually about 80 centimetres, or twice that of the iron tube. The outer tube was then drawn out at the open end, attached to the Sprengel pump, exhausted, and finally heated in a combustion furnace along that portion which was occupied by the iron tube. The quantities of magnesium employed in our experiments varied from 4.5 to 10 grms.; those of the oxide, from 1.5 to 3 grms.

In every case the phenomena which presented themselves when the tube had reached a bright red-heat were similar to those observed when the oxides of zinc and cadmium were heated with their metals. The oxide formed in the cool portion of the glass tube, and fell upon the bottom in a long line which extended even into the connecting tube of the pump itself. This transportation of the oxide continued until the greater portion of the metal had distilled to and condensed about the open end of the iron tube. At the same time gas was evolved and collected in the eudiometer placed over the outlet of the pump. This gas proved to be a mixture of carbon dioxide and free oxygen. The proportion of the oxide thus transported to the cooler portion of the glass tube was quite variable, and appeared to depend on the thoroughness with which the oxide and metal were mingled in the iron tube. It was always found to be greater when the mixture of oxide and metal which remained in the inner tube after one experiment was re-heated with an additional quantity of magnesium. It was not possible to determine

the exact amount of oxide which was carried out of the iron tube, owing to the presence in it of some distilled metal; but on several occasions that portion of the oxide which was nearest the pump, and appeared to be free from metal, was collected and weighed. The quantity varied from 0.1 gm. to 1.5 gm. In some cases only a small fraction of the oxide remained in the iron tube.

As in the case of the oxides of zinc and cadmium, the evolution of oxygen was most rapid during early stages of the experiment, before the tube had become filled with the vapours of the metal. The carbon dioxide, which must have come from the carbon contained in the iron, was removed by caustic potash, and the oxygen determined by means of an alkaline solution of pyrogallous acid. The quantity of oxygen found varied from 1.5 to 3 c.c.—*American Chemical Journal*, vol. xiii., p. 128.

Chemical Laboratory, Johns Hopkins University.

DETERMINATION OF AVAILABLE OXYGEN IN PEROXIDES BY MEANS OF GASEOUS HYDROCHLORIC ACID.

By L. L. DE KONINCK and AD. LECRENIER.

AMONG the procedures employed for the determination of the available oxygen of the manganese oxides, or for the determination of the peroxide in ores, the method of Bunten is very often preferred. The sample is treated with strong hydrochloric acid, and the chlorine liberated is received in a solution of potassium iodide. The iodine set free is then determined by means of a standard solution of sodium thiosulphate.

The hydrochloric acid is necessarily employed in considerable excess, and the necessity of raising the liquid to ebullition for a few minutes so as to expel all the chlorine liberated, causes a notable quantity of the acid to pass into the solution of potassium iodide, which falsifies the results if the titration with thiosulphate is not effected rapidly. In fact, the hydriodic acid formed is decomposed in contact with the oxygen of the atmosphere.

The authors have obtained results very satisfactory in every respect by using hydrochloric gas in place of the liquid acid.

The oxide in question is placed at the bottom of a flask with a small quantity of water (two or three parts to one of oxide), and when the different parts of the apparatus are connected and found air-tight, a very slow current of carbonic anhydride is introduced, followed by hydrochloric acid gas. The latter gas is absorbed by the water, and the solution of the sample and the liberation of chlorine begin immediately, favoured by the rise of temperature due to the absorption of the gas.

The reaction is accelerated by heating the bottom of the flask by means of a very small flame. In a few moments the solution is complete, and its greenish colour, due to manganese chloride, disappears, giving place, in case of natural oxides of manganese, to the yellow colouration of ferric chloride, or to a decided green, if the ore contains cobalt at the same time.

At this moment the entrance of the hydrochloric acid gas is stopped, whilst the rapidity of the current of carbonic anhydride is increased, and the solution in the flask is still heated.

When the hydrochloric acid has thus been entirely expelled, the apparatus is dismantled and the iodine set free is titrated.

It is necessary to use in the analysis a quantity of water such that the chlorides formed may not be deposited until after the solution has become cold, and at the same time too large an excess must be avoided. If the water is deficient a part of the oxide may become coated with a protective layer of chloride, or which renders the ulterior attack of the oxide very difficult.

As regards the quantity of the acid it is found that

when operating upon 0.3 to 0.4 gm. of oxide the quantity is 1.27 gm., corresponding to 5 c.c. of acid at 25 per cent. Of this quantity of acid about the half is utilised for the reaction, whilst the other half constitutes the excess which is absorbed by the solution.

The process is perfectly applicable to the determination of the available oxygen in samples of red lead. No modification is required in the process as just described. —*Revue Universelle des Mines*, Jan., 1891.

SEPARATION AND DETERMINATION OF NICKEL AND COBALT.

By CONSTANTIN KRAUSS.

(Continued from p. 264).

A FURTHER modification of the Liebig process consists in mixing the solution of both metallic salts with an excess of potassium cyanide, and boiling until no free hydrocyanic acid can be recognised. The nickel is then precipitated with bromine water, and the cobalt is determined in the filtrate.

Fr. Gauhe has carefully studied this modification, and has arrived at very satisfactory results.

According to a further modification of the Liebig process, H. Roser adds to a mixture of nickel and cobalt oxide first hydrocyanic acid and then ammonia, and heats to ebullition. He then boils with ammonium sulphide and sulphur until the deep black liquid becomes perfectly clear. All the nickel is thus precipitated as nickel sulphide, whilst all the cobalt remains in solution as ammonium cobaltcyanide.

This process also gives satisfactory results, but it has no advantage as compared with those just described, as the precipitate of nickel sulphide must be re-dissolved and again precipitated.

13. C. Roessler adds to the solution of a cobaltous salt a measured volume of a normal silver solution, and heats on the water-bath, adding sodium carbonate as long as a precipitate of $\text{Ag}_4\text{O}, \text{Co}_2\text{O}_3$ is produced. It is then digested with a little ammonia in order to dissolve any silver carbonate which has been carried down. The liquid is then filtered, and after acidulation with nitric acid the excess of silver is determined volumetrically by Volhard's process.

Krauss always obtained by this method deficient values. More favourable results appeared if caustic potassa, free from haloids, is used instead of sodium carbonate. In this case the method is applicable in presence of moderate quantities of nickel.

14. Clemens Winkler mixes a perfectly neutral solution of cobaltous chloride with elutriated mercuric oxide, and drops in the cold solution of permanganate, shaking the vessel continuously, until the liquid has a faint permanent rose colour. The cobalt separates out as hydroxide, $\text{Co}_2(\text{OH})_6$.

He uses a decinormal solution of cobalt (5.86 grms. cobalt per litre) and a solution of permanganate containing 5.27 grms. permanganate per litre.

According to the author's experiments, this method yields good results, whether the proportion of cobalt is very large or very small, especially if there is added from time to time a little mercuric oxide and a few drops of ferric chloride free from the ferrous salt.

The results are less favourable in presence of nickel. The author verifies Winkler's statement that for the proportion $\text{Co} : \text{Ni} = 1 : 4$ the results are just admissible in practice. In presence of nickel, the quantity of cobalt to be determined must not be too small—not less than 0.03 gm. If there is very little cobalt present, it is advisable previous to titration to add a measured volume of a normal cobalt solution, and to take this addition into account in calculating the results. The use of large quantities of cobalt is not advantageous; the most favourable results were obtained when from 0.075 to 0.1

gm. cobalt has to be determined, and a solution of permanganate is taken only half as strong as that proposed by Winkler.

The objection raised against this method in various quarters, i.e., that the mercuric oxide interferes with a recognition of the end of the reaction, is considered by Krauss as quite unfounded. The mercuric oxide, on the contrary, facilitates the reaction by carrying down the suspended cobalt oxychloride, and thus clearing the solution.

Gauhe's proposal, to add, when standardising the normal solution of cobalt, so much nickelous chloride that it may have the same shade of colour as the solution under examination, is regarded by Krauss as useless.

Good results, suitable for practical purposes, may be obtained in presence of a considerable proportion of nickel if during titration there are added from time to time a few c.c. of ferric chloride (free from ferrous chloride), shaking well and titrating, not up to a permanent red colouration, but merely to a rapid and complete clarification.

B.—Methods Depending on the Different Behaviour of the Sulphides of Both Elements.

1. H. Fleck (*Journ. Prakt. Chemie*) allows the solution of both metals, mixed with ammonium chloride and oversaturated with ammonium, to stand for twelve hours exposed to the air in a shallow capsule. He adds ammonium sulphide in excess, and evaporates on the water-bath until turmeric paper is no longer turned brown. When cold, he adds, at the lowest available temperature, a few c.c. of potassium cyanide, and allows the mixture to stand for some minutes. The precipitate formed is filtered and washed with alcohol at 80 per cent. By dissolving the ignited precipitate and re-precipitation with ammonia and ammonium sulphide, pure cobalt sulphide is obtained.

The nickel is precipitated from the filtrate as nickel cyanide by the addition of hydrochloric acid, and determined in the known manner.

This method, according to Krauss, gave no favourable results, as an appreciable quantity of cobalt sulphide passes into solution.

A. Guyard (*Bulletin de la Soc. Chimique*) recommends this method, but has not improved it in any manner.

2. C. Kunzel (*Journ. Prakt. Chemie*) proposes to titrate both metals with potassium sulphide in an ammoniacal solution.

Krauss standardised a solution of potassium sulphide (using sodium nitro-prusside as an indicator) by means of a known solution, both of nickel and cobalt. The results were very fluctuating, which was the more striking as more potassium sulphide was always used for cobalt than for an equal quantity of nickel. This fact renders it probable that the sulphides have no constant composition, a conjecture which the author supports by several experiments.

Definite quantities of cobalt and nickel were precipitated with potassium sulphide, avoiding any excess; the precipitates were filtered off, and washed with cold water. If the sulphides thus obtained were decomposed with ammoniacal solution of copper, or solution of silver, and the combined sulphur was determined, it was found that cobalt combines with a rather larger proportion of sulphur than does nickel. This unequal composition of the sulphides, joined to the fact that they are not absolutely insoluble in ammonia, renders the method of Kunzel nearly worthless.

(To be continued).

Centenary of the Birth of Michael Faraday.—H.R.H. The Prince of Wales has fixed 4 o'clock on Wednesday, the 17th June, for the delivery by Lord Rayleigh of the first of the two Lectures at the Royal Institution in connection with this Centenary; and Friday evening, the 26th June, at 9 o'clock, has been appointed for the second of these Lectures, which will be given by Professor Dewar.

EXPERIMENTS ON THE PRECIPITATION OF ANTIMONY FROM SOLUTIONS OF THE TARTRATE OF ANTIMONY AND POTASSIUM.*

By J. H. LONG and H. E. SAUER.

(Concluded from p. 270).

Precipitation by Sodium Acetate.

SOME instructive results were obtained in a series of tests with sodium acetate. With cold, dilute solutions, the precipitation is very slow, but on application of heat it becomes quite marked. In the next table are given the results found by adding to a solution of the tartrate (5 grms.) solutions of different amounts of the acetate. The mixtures were carefully made and diluted to 100 c.c. at 20°, and were then allowed to stand 48 hours. In the first experiment (No. 24) only an opalescence appeared in that time, but in the other cases the mixture soon became cloudy, to precipitate and settle long before the end of the 48 hours. The clear supernatant liquids were then filtered off, the filtrate and washings in each case being diluted to 250 c.c. The antimony was determined in 50 c.c. and calculated as tartrate, the results being shown in the last column.

100 c.c. at 20°. Filtrate Made to 250 c.c.

No.	Amount of KSbOT. Grms.	Amount of NaC ₂ H ₃ O ₂ . Grm.	Sb ₂ S ₃ in 50 c.c. Grm.	Per cent of KSbOT taken in solution.
24.	5	2	trace	(100)
25.	5	5	0.439	86.77
26.	5	10	0.454	89.72
27.	5	15	0.460	90.90

These numbers show that in the cold precipitation by the acetate is far from complete. It also appears that while a small amount of the acetate does not produce actual precipitation, a large excess gives less precipitation than does a much smaller amount. It is possible that the excess of acetate exerts a solvent action on antimonious hydroxide, which we may look upon as precipitated in the first stage of the reaction, or it may be that a new soluble compound is formed by double decomposition in this manner:—



Free acetic acid has the power of dissolving a small amount of the precipitate, Sb₂O₃.H₂O, as we found by a series of experiments. We also found that a well-washed precipitate of this composition was slightly dissolved by gently warming with a solution of sodium acetate.

Acetates of antimony are scarcely mentioned in the literature, yet these experiments and others speak for their existence.

The polarisation tests of the solutions of tartrate and acetate, mixed in the cold, show a steady decrease in the rotation with increase in the amount of added acetate, suggesting a progressive decomposition of the tartrate. With 2 grms. of acetate in solution only faint opalescence is produced, while with 5 grms. a marked precipitate is formed. As this precipitate decreases with further addition of acetate it is possible that for some amount between the 2 and 5 grms. it is a maximum.

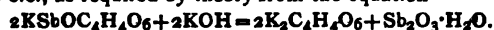
With elevation of temperature, all this is changed, however. (See table below.)

100 c.c. at 100°. Filtrate Made to 250 c.c.

No.	Amount of KSbOT. Grms.	Amount of NaC ₂ H ₃ O ₂ . Grm.	Sb ₂ S ₃ from 50 c.c. Grm.	Per cent of KSbOT taken in solution.
28.	5	2	0.438	86.56
29.	5	5	0.381	75.30
30.	5	10	0.312	61.66
31.	5	15	0.291	57.50

* From the *Journal of Analytical and Applied Chemistry*, v., No. 3.

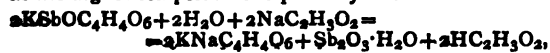
Now 2 grms. of the acetate gives a good precipitate, and the amount of antimony thrown down from solution increases with added acetate. After heating a solution of 5 grms. of tartrate and 10 grms. of the acetate for an hour on the water-bath, the presence of free acetic acid was readily shown in the filtrate by titration with half normal KOH and phenol-phthalein. No turbidity was produced in the solution until nearly 12 c.c. of the alkali had been added, and the colour appeared, on addition of 30 c.c., as required by theory from the equation—



When alkali is added to a mixture of acetate and tartrate, prepared in the cold, a precipitate forms immediately and grows heavier with increase of the precipitant. Alkali, in absence of the acetate, produces a turbidity, but no actual precipitate at the start.

These facts seem to lead to the conclusion that at low temperatures antimony forms a stable and soluble compound with acetic acid which is decomposed with precipitation of the antimony and liberation of the acid at a higher temperature.

The 12 c.c. of half normal KOH added to the filtrate from the boiled solution before an opalescence appeared, indicated that two-fifths of the tartrate had been decomposed, which corresponds closely to what is found by determination of the antimony in No. 30. The reaction at the higher temperature is probably this—



and the first alkali added simply combines with the free acetic acid. The amount subsequently added decomposes either the tartrate, $\text{KSbOC}_4\text{H}_4\text{O}_6$, in the manner indicated by an equation above, or an intermediate product, possibly $\text{SbOC}_2\text{H}_3\text{O}_2$.

The manner of precipitation strongly suggests the existence of such a product.

Precipitation by Sodium Phosphate.

Solutions of phosphates precipitate the potassium antimony tartrate in the same general manner, but the reaction appears to require a longer time for its completion. We made experiments with a number of solutions, the chief results of which are given below.

In these examples the solutions were made hot, mixed, and kept in the water-bath one hour. The filtrates obtained were strongly acid, and their behaviour on titration suggested presence of free phosphoric acid, which could be liberated in this manner—



100 c.c. at 100°.

No.	Amount of $\text{KSbOC}_4\text{H}_4\text{O}_6$ Grms.	Amount of HN_3PO_4 Grms.	Sb_2O_3 from 50 c.c. Grms.	Per cent of $\text{KSbOC}_4\text{H}_4\text{O}_6$ taken in solution.
32.	5	0.2	1.234	97.56
33.	5	0.5	1.1930	94.32
34.	5	0.8	1.1370	89.89
35.	5	2.0	0.9335	73.77
36.	5	5.0	0.6379	50.43
37.	5	10.0	0.3851	30.52
38.	5	15.0	0.3192	25.24

Cold solutions can be mixed without producing precipitation, even when 1 gm. of the phosphate is present. Solutions so made were examined with the polariscope, which showed that the large rotation characteristic of the tartrate was very much diminished, probably by some decomposition in the active molecule. This behaviour can be accounted for by assuming the existence of a preliminary reaction in which the antimony, in part at least, is held in an unstable form by the phosphoric acid.

It will be seen from the table that the precipitating power of the phosphate is much more marked than that of the acetate, while both fall short of the carbonate. A

few tests were made with solutions of borax as a precipitant, but quantitative results were not obtained. We observed also that solutions of several other oxygen salts are unable to precipitate the antimony. This appears to be true of sulphates, nitrates, and oxalates—at all events with solutions of moderate concentration. Cold mixtures of the tartrate with sodium hypophosphite and sodium sulphite precipitate very slowly, but if heated, decomposition begins soon. Even with sodium thiosulphate, some time elapses before a precipitate forms, which finally, after heating, appears to consist wholly of sulphide.

The reasons for these differences in behaviour are not immediately apparent. The problem is complex, as we have at least four factors to deal with, viz., mass, concentration, time, and temperature. It was shown by one of us by polariscopic observations (*loc. cit.*) that long before a precipitate is visible in these solutions, a change has begun, and that this change is a progressive one. A solution of 5 grms. of the tartrate with 0.5 gm. of sodium carbonate, if carefully made and kept at a low temperature, remains perfectly clear during 24 hours or longer; so clear that it can be examined in a polarisation tube 400 m.m. in length. Observations made at intervals through the 24 hours show a gradual and marked decrease in the angular rotation of the solution. Finally, a precipitate forms and separates out, but the change in the rotation, for a given temperature, is probably completed independently of this. Actual precipitation must, therefore, be preceded by a stage of preparation, which, in some cases, may be prolonged almost indefinitely.

As a further contribution to the subjects of these precipitations, we have in mind the study of the behavior of several other salts.

Chicago, March, 1891.

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, June 1, 1891.

SIR JAMES CRICHTON-BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

The following were elected Members of the Royal Institution:—R. W. Peregrine Birch; William Edmonds; Nicholas Eumorfopoulos; Mrs. Charles Hoare; Mrs. Edward Singleton; and Harold Swinbank.

The special thanks of the Members were returned for the following donation to the Fund for the Promotion of Experimental Research:—

Mrs. Priestley £21.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

NOTICES OF BOOKS.

The Romance of Science Series. Colour-Measurement and Mixture. By CAPTAIN W. DE W. ABNEY, C.B., R.E., F.R.S. Published under the direction of the Committee of General Literature and Education appointed by the Society for Promoting Christian Knowledge. London: Society for Promoting Christian Knowledge, Northumberland Avenue, W.C.

COLOURS are undoubtedly a subject most interesting not merely to the man of science, but to the general outside public. It must further be at once recognised that there are very few authorities capable of expounding the laws of colour so ably as Captain Abney. It may perhaps

however, be questioned whether the author has not approached his subject too much from the point of view of the mathematician-physicist. That he should do so is, of course, in perfect accordance with the special title of the volume, "Colour Measurement and Mixture"; but many readers will think that a greater prominence given to the chemical and biological phase of the subject would have been more in keeping with the general title of the series.

Captain Abney recognises three "colour constants," viz., hue, luminosity, and purity. What is here called "hue" is generally spoken of in the tinctorial arts as "tint," e.g., the modification in a blue solution or pigment according as it approaches to or receives from a red on the one hand or a green on the other.

As a standard light, the author for sound reasons dismisses the sunlight as a standard, as well as gaslight, the limelight, and the glow-lamp. He prefers the arc-light. Concerning the magnesium light he does not pronounce an opinion. He finds the prismatic spectrum more convenient than the diffraction spectrum which gives only about one-third of the light. A list of the principal colours in the spectrum, drawn up by Prof. Rood, gives ten gradations in place of the ordinary seven.

The demonstration of the existence of the ultra violet and infra-red rays invisible to the human eye will be found very interesting. In a succeeding chapter the spectral diagnosis of colours which appear identical to the eye is very clearly demonstrated. The origin of sunset colours and of the luminosities of sunlight at different altitudes is also made fully intelligible.

In chapter xi. we find it shown why and how red, yellow, and blue, were formerly recognised as the primary colours, and in what lay the error of the observers. The present three-colour theory (red, green, and violet), was, as most of our readers know, due to Thomas Young, and was revived by Clerk-Maxwell and Helmholtz. Some of us may have met with the plausible but fallacious essay in which Lord Brougham, Chancellor and Sciolist, sought to demolish this theory. In speaking of colour-blindness Captain Abney wisely points out that in the registration of cases of colour-blindness the eye of the observer ought first to be tested.

This book will amply repay a careful perusal.

Practical Work in Organic Chemistry. By FREDK. WM. STREATFIELD, F.I.C., &c., Demonstrator of Chemistry at the City and Guilds of London Institute's Technical College, Finsbury. With a Prefatory Notice by PROF. R. MELDOLA, F.R.S., Foreign Secretary of the Chemical Society. London and New York: E. and F. N. Spon.

This work forms a member of the series of "Finsbury Technical Manuals," issued by Messrs. Spon under the general editorship of Professor Silvanus Thompson. It is totally distinct from the elementary manuals of chemistry now so numerous. The laboratory work here proposed—after a general elementary foundation has been laid—has been divided into a series of programmes arranged to meet the demands of the various chemical industries, and which fairly cover the elementary principles involved in those arts in which organic chemistry is concerned. Prof. Meldola, however, very wisely recommends the student, if his time permits it, to work through all the programmes so as to acquire a wider range of practical knowledge.

A few remarks made by Prof. Meldola on the general working of the Finsbury Technical College are too important, and, we may add, too encouraging to be passed over. He tells us that during the six years of his connection with the Finsbury College there has been "a steady increase in the number of evening students." He is convinced by "the zeal with which men who are engaged in all day, often in very arduous occupations, will carry on

supplementary work in the evening hours that such instruction supplies a distinct want." The real value of the training obtained at the City and Guilds of London Institute is "amply shown by the numerous records of promotion or improved position which the evening students have been enabled to take. Another favourable sign is the fact that a considerable number of day-students who have completed their courses and have obtained appointments in the London district, re-enter the College as evening students."

Another and still more valuable symptom is "the fact that the competition produced by the spread of the Polytechnic movement has had no appreciable effect upon the evening attendance, and this in spite of the fact that we cater for no examination."

This is doubly important: it shows that there are still young men who study to know and not to "pass," and that there are still employers who can and do recognise ability even when unaccompanied by the certificate of any board of examiners.

The work contains, first, instructions on the performance of the more general operations, and directions for organic analysis, in which, however, we find no mention of the Kjeldahl process for the determination of nitrogen; then follow the four programmes, the study of oxalic acid and its reactions, ethyl alcohol and its reactions, the preparation and decomposition of ethyl acetate and of the composition and reactions of some natural fats and oils, and, lastly, coal-tar and coal-tar products.

This book must be pronounced an excellent guide for the careful and conscientious student.

Elements of Crystallography for Students of Chemistry, Physics, and Mineralogy. By G. HUNTINGDON WILLIAMS, Ph.D., Associate Professor in the Johns Hopkins University. Second edition, revised. London: Macmillan and Co.

CRYSTALLOGRAPHY is a subject which attracts but few students. Of course the mineralogist can make little progress without he is able to express the forms of the substances which come under his consideration. But mineralogy itself is not a very popular study.

Prof. Williams commences his work with a bibliography of the subject, in which we find not a single English name and only two American.

We learn that the scope of this book embraces only geometrical crystallography, leaving the physical and chemical consideration of crystals untouched. After general remarks on crystalline structure, and an account of the general principles of crystallography, he takes up in succession the isometric, the tetragonal, hexagonal, orthorhombic, monoclinic, and triclinic systems, and discusses aggregates and the imperfections of crystals.

An appendix treats of zones, projection, and the construction of crystal figures. In speaking of crystallographic notation the author mentions the symbols of Weiss, Naumann, and Miller (Whewell). Griffin's system is not referred to at all.

We may perhaps hope that the volume before us may extend the study of crystallography.

CORRESPONDENCE.

CONDY'S FLUID.

To the Editor of the Chemical News.

SIR,—We shall esteem it a favour if you will kindly inform your readers that we have just obtained a second injunction in the United States against a person who has used the designation Condy's Fluid for a fluid not manufactured by us.

Five injunctions have been granted in this country

against persons selling colourable imitations of Condy's Fluid.

We beg to enclose particulars of some of these judgments.—We are, &c.,

H. J. BOLLMAN CONDY.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxii., No. 21, May 25, 1891.

Researches on the Camphenic Series.—MM. Berthelot and Matignon.—A thermo-chemical study of a class of carbides isomeric with oil of turpentine, and which generate camphor and borneol. The authors consider that their observations throw a new light on chemical combination, and on the fundamental truth that atomicity does not pre-exist in an absolute manner in the elements or components of a compound, but is manifested in the finished compound and in the type which it realises.

On the Tensions of Saturated Watery Vapour up to the Critical Point, and on the Determination of this Critical Point.—L. Cailletet and E. Colardeau.—The contents of a "sealed paper" deposited June 23, 1890. This memoir cannot be reproduced without the accompanying figure and diagram.

The Analysis of Light Diffused by the Sky.—A. Crowe.—The blue of the sky, as observed in England by Lord Rayleigh, is more saturated than that observed at Potsdam by Prof. Vogel. The blue of the sky observed by the author at Montpellier, in January, 1890, is deeper than those observed in England and Germany.

Relation between Atomic Weight and Liquid Density.—Al. Moulin.—The author's results are given in the form of tables.

On Argentous Chloride.—M. Guntz.—According to the temperature at which it is produced the argentous chloride (silver subchloride) varies in colour from deep violet-red to a black-violet. The action of light tends to produce the black modification without a loss of chlorine. By the action of heat the subchloride is decomposed, turning pale yellow, and leaving silver and silver chloride. The action of dilute nitric acid (1 eq. = 2 litres) is absolutely null; thus 50 c.c. of dilute nitric acid left for 24 hours in contact with 2 grms. Ag_2Cl gave no appreciable turbidity on the addition of a solution of sodium chloride. Strong nitric acid reacts upon argentous chloride, especially in heat, yielding silver chloride more or less mixed with subchloride and forming lakes of various colours (Carey Lea's photochlorides).

Action of the Presence of the Mineral Salts of Potassium on the Solubility of Potassium Chlorate.—Ch. Blarez.—Saturated solutions of potassium chlorate, mixed with caustic potassa or a soluble salt of potassium, cause a part of the chlorate which was dissolved to pass out of solution.

Electrolysis of the Salts of Boron and Silicon of Igneous Fusion.—Adolphe Minot.—The author refers to the experiments of H. Sainte-Claire Deville, who decomposed a double aluminium and sodium chloride containing a little silicon, and obtained a grey casting composed of an alloy of aluminium and silicon. He substitutes for the aluminium salt used by Deville a mixture of sodium chloride (60 parts) and double aluminium and sodium fluoride (30 parts). To the salts, at the instant of their fusion, he adds alumina and silica, 5 parts of each. The bath is contained in a cast-iron

crucible lined with carbon, which serves as a cathode. The anodes consist of plates of carbon agglomerate. It is maintained at a temperature of 850° . The operation is divided into seven periods, the density of the current being gradually raised from 0.15 to 1 ampère, and the electromotive force from 0.54 to 2.50 volts. In this manner, by operating upon bauxites and natural aluminium silicates, it is practicable to produce the entire series of alloys of iron—silicon, aluminium, and, finally, chemically pure aluminium. Alloys containing 8.9 per cent of silicon are found superior to pure aluminium.

On Two New Crystalline Combinations of Platinum Chloride with Hydrochloric Acid.—Leon Pigeon.—The compound of platinic chloride with hydrochloric acid, previously known under the name chloroplatinic acid, is represented by the formula $\text{PtCl}_4 \cdot 2\text{HCl} \cdot 6\text{H}_2\text{O}$. The two newly-discovered compounds are—



The first is obtained by dissolving the red crystals of chloroplatinic acid in a small quantity of water and adding a large quantity of sulphuric acid, when a yellow precipitate is deposited. The second compound is obtained by heating chloroplatinic acid to 100° in a vacuum in presence of melted potassa.

On Bismuth Salicylate.—H. Causse.—This compound is a neutral salicylate with 4 mols. of crystalline water. It forms colourless microscopic prisms, very similar to dehydrated quinine sulphate. It is insoluble in water, and is readily decomposed by acids and alkalis.

On the Solution-Heat and the Solubility of certain Bodies in the Methylic, Ethylic, and Propylic Alcohols.—W. Timifew.—A thermo-chemical paper, not adapted for useful abstraction.

Bulletin de la Société Chimique de Paris. Series 3, Vol. v., No. 7.

Preparation and Properties of Silver Fluoride.—Henri Moissan.—The author first prepares silver carbonate by precipitating pure silver nitrate in a dilute solution with solution of sodium bicarbonate. The precipitate is washed by decantation with abundance of distilled water. The thick deposit is placed in a platinum capsule, and hydrofluoric acid free from silver is added. The liquid is rapidly evaporated, at first over an open fire. When crystallisation has commenced the capsule is placed on a sand-bath, and the mass is stirred with a spatula until it is completely dry. The black pulverulent residue dissolves easily in water. It is filtered; the solution is placed in a platinum capsule, and evaporated in a vacuum with exclusion of light over sulphuric acid. There is thus obtained a light yellow mass, tough and elastic. Its fusion-point is 435° . It reacts very energetically upon the non-metallic chlorides.

Action of Hydrofluoric Acid upon Phosphoric Anhydride. Preparation of Phosphorus Oxyfluoride.—Henri Moissan.—The author confirms the remark of Prof. Thorpe, that Mallet's reaction must produce phosphorus oxyfluoride, and not pentafluoride. When hydrofluoric acid, perfectly dry, and kept in the gaseous state at a temperature above 19.5° , is passed over phosphoric anhydride, the latter becomes hot and a gaseous body is given off, PF_3O_2 . This gas is at once decomposed on contact with water. Its sp. gr. is 3.72, the theoretic density of phosphorus oxyfluoride being 3.63. Hence phosphoric acid must never be employed for drying hydrofluoric acid.

Transformation of Starch into Dextrine by the Butyric Ferment.—A. Villiers.—The author considers that further researches are needed to decide if the dextrines which he has obtained are identical with those produced by the action of acids or of diastase.

The Fermentation of Starch by the Action of the Butyric Ferment.—A. Villiers.—Not merely potato-

starch, but other starches ferment under the same conditions under the action of the butyric ferment. The resulting products are not always identical.

On Cotton-Dyeing.—Leo Vignon.—The author has shown that if silk, wool, and cotton are immersed in acid, alkaline, or saline liquids of known compositions, and placed in the calorimeter, they give rise to definite, constant, and measurable thermic phenomena. He has tried to modify the molecule of cotton so as to confer on it given chemical functions, and has then sought in what extent its tinctorial properties were changed. Schutzenberger and Thenard have shown that a number of non-nitrogenous substances are capable of fixing nitrogen in forms other than the ammoniacal. The author's samples, after being nitrogenised, were found capable of taking up considerable proportions of acid colouring-matters.

Influence of Hydrofluoric Acid and Fluorides upon the Activity of Yeast.—Dr. J. Effront.—Fluorides increase the activity of yeast when it is in excess, and produce a maximum effect when insufficient quantities of yeast have been employed.

Use of Manganese Sulphide as a Pigment.—Ph. de Clermont and R. Guiot.—The authors render the colour of the green sulphide permanent by removing the water of hydration. This is done by heating it gently in a current of hydrogen sulphide, of carbon dioxide, or of ammonia.

The Formation of the Iso-purpurates.—Raoul Varet.—Silver, mercury, or copper cyanides do not react upon picric acid or the picrates so as to form an iso-purpurate. Zinc cyanide, on the contrary, does so react, but much more slowly than the alkaline cyanides.

Vol. v., No. 8.

The Column which Emerges in the Measurement of Temperatures with the Mercurial Thermometer.—Ch. Ed. Guillaume.—The author proposes the following correction for that part of the mercurial column which emerges from the bulb, and is generally at a lower temperature— $c = n \alpha (T - r)$; n signifies the number of degrees not exposed to the temperature of the bulb; α the coefficient of the relative expansion of the mercury in the glass, about 0.00016; T the temperature sought for; r the mean temperature of the n degrees which emerge. If, e.g., the temperature sought is 400°, the number of degrees emerging 350, and their mean temperature 20°, we have $c = 350 : 0.00016 (400 - 20) = 21.3$. The difficulty lies in the determination of r .

A Contribution to the Study of the Production of Urea.—Dr. Popoff.—The transformation of ammoniacal salt into urea in the animal economy cannot be ascribed to the action of a soluble ferment, but results from a function of the living cell.

Researches on Derivatives of Xylose.—G. Bertrand.—Xylite cannot be combined with ethylic aldehyd. Numerous attempts to obtain a benzoic or ethylic acetal with the product of the hydrogenation of arabinose have completely failed. This is a character which completely distinguishes arabinose and xylose.

The Theory of the Phenomena of Dyeing.—Leo Vignon.—The author has shown by the thermo-chemical method that animal textile fibres which can be dyed readily possess basic or acid functions, whilst vegetable fibres having little aptitude for dyeing manifest very feeble chemical functions, and especially no basic functions. Cotton, if submitted to the action of ammonia, fixes nitrogen, acquires basic functions, and becomes able to absorb acid colouring-matters in an acid bath. Stannic acid fixes basic colouring-matters such as saffranine, whilst metastannic acid—which is merely stannic acid polymerised, having undergone a great attenuation in its acid functions—exerts no absorbent power upon saffranin. All soluble colouring-matters, artificial or natural, contain either a salifiable group, OH, or the basic groups, NR₂,

or the acid radicles, NO₂. We know no colouring-matter consisting solely of a carbide, or possessing no other chemical functions than those of an alcohol, acetose, or aldehyd. All the phenomena of dyeing obtained with soluble colouring-matters necessitate two essential conditions:—(1) The presence of acid or basic functions in the absorbents; (2) The presence of the same functions in the colouring-matters. The sole provisional exception to this rule is that of the tetrazo-dyes.

The following papers, all by M. Berthelot, have appeared in the *Comptes Rendus*, and have been noticed in due course. We submit that if a paper is read before two societies, or sent for insertion to two journals, the fact should be distinctly mentioned.

On the Explosion Wave.

On the Relations between the Change of Volume, the Stability of Compounds, and the Heat liberated in Chemical Reactions.

On Photo-Chemical Actions.—Action of Heat upon Carbon Monoxide.

A Reaction of Carbon Monoxide.

The Determination of Mineral Matters contained in Vegetable Soil, and their Function in Agriculture.

The Presence and the Function of Sulphur in Plants.

New Observations on the Volatile Nitrogenous Compounds emitted by Vegetable Soil.

On the Specific Odour of the Soil.

The Preparation of Pure Hydrogen.

History of Chemical Science in the Middle Ages.

Vol. v., No. 9.

Facts toward the History of the Nitrogenous Principles contained in Vegetable Mould.—MM. Berthelot and André.—The insoluble nitrogen contained in the humic compounds may be gradually rendered assimilable. The actions of plants are certainly not identical with those presented by acids and alkalies in our experiments. Nevertheless they are comparable as regards the chemical mechanisms brought into play by the earthy carbonates and carbonic acid, as well as by the acids formed in plants.

The Reactions of the Oxyalkoylic Derivatives of Dimethylaniline.—Edouard Grimaux.—The author seeks to establish the function of the oxyalcoholic groups, such as oxymethyl, OCH₃, oxyethyl, OC₂H₅, substituted in the nucleus C₆H₅, of dimethylaniline; and to trace, at the same time, the difference of reaction of the bases according to the place which these groups occupy with respect to N(CH₃)₂. The author has studied the meta and ortho bases: the properties and reactions of these bases will be described *in extenso*.

Antiseptic Properties of Sulphonic Amethyl-camphophenol.—P. Cazeneuve and M. Rodot.—The substance in question is but slightly antiseptic. Experiments on animals prove that it is not absolutely poisonous.

On the Pyrogenous Transformation of the Campho-sulphophenols into Homologues of Ordinary Phenols.—P. Cazeneuve.—Not adapted for useful abridgment.

The Falsifications of Bees' Wax and their Detection.—A. and P. Buisine.—This memoir will be inserted *in extenso*.

Revue Universelle des Mines et de la Metallurgie.
Vol. xiii., No. 1.

Determination of Available Oxygen in Peroxides by means of Gaseous Hydrochloric Acid.—Prof. L. L. de Koninck and Ad. Lecrenier.—(See p. 280).

Iodometric Determination of Nitrates and Chlorates.—L. L. de Koninck and Ed. Nibouk.—This paper will also be inserted *in extenso*.

February, 1891.

This issue does not contain any chemical matter.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vi., No. 61.

This issue does not contain any chemical matter.

Archives Néerlandaises des Sciences Exactes et Naturelles. Vol. xxv., Part 5.

This issue is entirely taken up with mathematical papers.

MEETINGS FOR THE WEEK.

WEDNESDAY, 17th.—Royal Institution, 4. (Faraday Commemoration Lecture). The Rt. Hon. Lord Rayleigh, M.A., F.R.S.

Microscopical, 8.
Meteorological, 7.

THURSDAY, 18th.—Royal, 4.30.
Chemical, 8. Ballot. "The Action of Sulphuric Acid on Dehydracetic Acid," by N. Collie.
"The Refractive Power of certain Organic Compounds at Different Temperatures," by Dr. W. H. Perkin, F.R.S.

FRIDAY, 19th.—Quekett, 8.

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THE CHEMICAL NEWS.

VOL. LXIII., No. 1647.

ON ELECTRICAL EVAPORATION.*

By WILLIAM CROOKES, F.R.S.

It is well known that when a vacuum tube is furnished with internal platinum electrodes, the adjacent glass, especially near the negative pole, speedily becomes blackened, owing to the deposition of metallic platinum. The passage of the induction current greatly stimulates the motion of the residual gaseous molecules; those condensed upon and in the immediate neighbourhood of the negative pole are shot away at an immense speed in almost straight lines, the speed varying with the degree of exhaustion and with the intensity of the induced current. Platinum being used for the negative pole, not only are the gaseous molecules shot away from the electrode, but the passage of the current so affects the normal molecular motions of the metal as to remove some of the molecules from the sphere of attraction of the mass, causing them to fly off with the stream of gaseous molecules proceeding from the negative pole, and to adhere to any object near it. This property was, I believe, first pointed out by Dr. Wright, of Yale College, and some interesting experiments are described by him in the *American Journal of Science and Arts*.† The process has been much used for the production of small mirrors for physical apparatus.

This electrical volatilisation or evaporation is very similar to ordinary evaporation by the agency of heat. Cohesion in solids varies according to physical and chemical constitution; thus every kind of solid matter requires to be raised to a certain temperature before the molecules lose their fixity of position and are rendered liquid, a result which is reached at widely different temperatures. If we consider a liquid at atmospheric pressure,—say, for instance, a basin of water in an open room,—at molecular distances the boundary surface between the liquid and the superincumbent gas will not be a plane, but turbulent like a stormy ocean. The molecules at the surface of the liquid dart to and fro, rebound from their neighbours, and fly off in every direction. Their initial velocity may be either accelerated or retarded, according to the direction of impact. The result of a collision may drive a molecule in such a direction that it remains part and parcel of the liquid; on the other hand, it may be sent upwards without any diminution of speed, and it will then be carried beyond the range of attraction of neighbouring molecules and fly off into and mingle with the superincumbent gas. If a molecule of the liquid has been driven at an angle with a velocity not sufficient to carry it beyond the range of molecular attraction of the liquid it may still escape, since, in its excursion upwards, a gaseous molecule may strike it in the right direction, and its temporary visit may be converted into permanent residence.

The intrinsic velocity of the molecules is intensified by heat and diminished by cold. If, therefore, we raise the temperature of the water without materially increasing that of the surrounding air, the excursions of the molecules of the liquid are rendered longer and the force of impact greater, and thus the escape of molecules into the upper region of gas is increased, and we say that evaporation is augmented.

If the initial velocities of the liquid molecules can be increased by any other means than by raising the tem-

perature, so that their escape into the gas is rendered more rapid, the result may be called "evaporation" just as well as if heat had been applied.

Hitherto I have spoken of a liquid evaporating into a gas; but the same reasoning applies equally to a solid body. But whilst a solid body like platinum requires an intense heat to enable its upper stratum of molecules to pass beyond the sphere of attraction of the neighbouring molecules, experiment shows that a very moderate amount of negative electrification superadds sufficient energy to enable the upper stratum of metallic molecules to fly beyond the attractive power of the rest of the metal.

If a gaseous medium exists above the liquid or solid, it prevents to some degree the molecules from flying off. Thus both ordinary and electrical evaporation are more rapid in a vacuum than at the ordinary atmospheric pressure.

I have recently made some experiments upon the evaporation of different substances under the electric stress.

Evaporation of Water.—A delicate balance was taken, and two very shallow porcelain dishes were filled with acidulated water and balanced on the pans. Dipping into each dish—touching the liquid but not the dish—was a platinum wire, one connected with the induction coil and the other insulated. The balance was left free to move, but was not swinging, the pointer resting at the centre of the scale. The water in connection with the coil was first made positive. After 1½ hours there was scarcely any difference between the weight of the insulated water and that which had been exposed to the positive current. Equilibrium being restored, the current was reversed, the negative current being kept on the dish for two hours. At the end of this time the electrified water was decidedly lighter. After having again restored equilibrium, the electrification of the dishes was reversed, i.e., the one that had before been insulated was made negative and the other one was insulated. In an hour the electrified water had become decidedly lighter than the insulated water. The experiment was performed in a room of uniform temperature, and any draught was prevented by the glass case of the balance. In a subsequent experiment in which the quantities were weighed, it was found that negatively electrified water lost in 1½ hours 1/10th part of its weight more than did insulated water.

This experiment shows that the disturbing influence which assists evaporation is peculiar to the negative pole even at atmospheric pressures.

The metal cadmium was next experimented upon.

A U-shaped tube was made, having a platinum pole sealed in each end. 6 grains of pure cadmium were put in each limb and fused round the platinum wire. The ends of the tube were then put into an air bath, and kept at a temperature of 200° C. during the continuance of the experiment. The exhaustion remained at 0.00076 m.m., or 1 M. The induction current was kept going for thirty-five minutes. At the end of this time it was seen that most of the cadmium had disappeared from the negative pole, leaving the platinum wire clean, no metal being deposited near it, and the molecules appearing to have been shot off to a distance of about ¼ inch. The appearance of the positive pole was very different; scarcely any of the cadmium had been volatilised, and the condensed metal came almost close to the pole. The tube was opened, and the remaining wires and metal were weighed. The cadmium was then dissolved off the poles in dilute acid; the residue was washed, dried, and weighed.

	Positive pole.	Negative pole.
Original weight of cadmium ..	6.00 grs.	6.00 grs.
Cadmium remaining on the pole	3.65 "	0.25 "

Cadmium volatilised in 35 mins. 2.35 " 5.75 "

The difference between the amount of cadmium driven from the two poles having proved to be so decided,

* Cadmium melts at 320° and boils at 860°.

* A Paper read before the Royal Society, June 11, 1891.
† Third Series, vol. xli., p. 49, January, 1877; and vol. xiv., p. 169, September, 1877.

another experiment was tried in a tube so arranged that the metal could be more easily weighed before and after the experiment. For this purpose a tube was blown U-shaped, having a bulb in each limb. The platinum poles were, as before, at the extremities of each limb, and in each bulb was suspended from a small platinum hook a small lump of cadmium, the metal having been cast on to the wire. The wires were each weighed with and without the cadmium. The tube was exhausted, and the lower half of the tube was enclosed in a metal pot containing paraffin wax, the temperature being kept at 230°C. during the continuance of the experiment. A deposit around the negative pole took place almost immediately, and in five minutes the bulb surrounding it was opaque with deposited metal. The positive pole with its surrounding luminosity could be easily seen the whole time. In thirty minutes the experiment was stopped, and after all was cold the tube was opened and the wires weighed again. The results were as follows:—

	Positive pole.	Negative pole.
Original weight of cadmium ..	9.34 grs.	9.38 grs.
Weight after experiment ..	9.25 "	1.86 "
Cadmium volatilised in 30 mins.	0.09 "	7.52 "

Finding that cadmium volatilised so readily under the action of the induction current, a large quantity, about 350 grs., of the pure metal was sealed up in a tube, and the end of the tube containing the metal was heated to a little above the melting-point; the molten metal being made the negative pole, in a few hours the whole quantity had volatilised and condensed in a thick layer on the far end of the tube, near, but not touching, the positive pole.

Volatilisation of Silver.—Silver was the next metal experimented upon. The apparatus was similar to that used for the cadmium experiments. Small lumps of pure silver were cast on the ends of platinum wires, and suspended to the inner ends of platinum terminals passing through the glass bulb. The platinum wires were protected by glass, so that only the silver balls were exposed. The whole apparatus was enclosed in a metal box lined with mica, and the temperature was kept as high as the glass would allow without softening. The apparatus was exhausted to a dark space of 3 m.m., and the current was kept on for 1½ hours. The weights of silver before and after the experiment, were as follows:—

	Positive pole.	Negative pole.
Original weight of silver ..	18.14 grs.	24.63 grs.
Weight after the experiment	18.13 "	24.44 "
Silver volatilised in 1½ hours	0.01 "	0.19 "

It having been found that silver volatilised readily from the negative pole in a good vacuum, experiments were instituted to ascertain whether the molecules of metal shot off from the pole were instrumental in producing phosphorescence. A glass apparatus was made as follows:—A pear-shaped bulb of German glass has, near the small end, an inner concave negative pole, of pure silver, so mounted that its inverted image is thrown upon the opposite end of the tube. In front of the pole is a screen of mica, having a small hole in the centre, so that only a narrow pencil of rays from the silver pole can pass through, forming a bright spot of phosphorescence at the far end of the bulb. The exhaustion was pushed to a high point, 0.00068 m.m., or 0.9 M. The current from an induction coil was allowed to pass continuously for some hours, the silver pole being kept negative, so as to drive off a certain portion of the silver electrode. On subsequent examination it was found that the silver had all been deposited in the immediate neighbourhood of the pole, whilst at the far end of the tube the spot that had been continuously glowing with phosphorescent light was practically free from silver.

An egg-shaped tube was next made, having two negative poles connected together, so placed as to project two luminous spots on the phosphorescent glass of the tube. One of the electrodes was of silver, a volatile metal; the other was of aluminium, practically non-volatile. On connecting the two negative poles with one terminal of the coil, and the positive pole with the other terminal, it was seen in the course of half an hour that a considerable quantity of metal had been projected from the silver negative pole, blackening the tube in its neighbourhood, while no projection of metallic particles took place from the aluminium positive pole. During the whole time of the experiment, however, the two patches of phosphorescent light opposite the two negative poles had been glowing with exactly the same intensity, showing that the active agent in effecting phosphorescence was not the molecules of the solid projected from the poles, but the residual gaseous particles, or "radiant matter."

In the tubes hitherto made containing silver, it had not been easy to observe the spectrum of the negative pole, owing to the rapid manner in which the deposit obscured the glass. A special tube was therefore devised, of the following character:—A silver rod was attached to the platinum pole at one end of the tube, and the aluminium positive pole was at the side. The end of the tube opposite the silver pole was rounded, and the spectroscopic was arranged to observe the light of the volatilising silver "end on." In this way the deposit of silver offered no obstruction to the light, as none was deposited except on the sides of the tube surrounding the silver. At a vacuum giving a dark space of about 3 m.m. from the silver, a greenish-white glow was seen to surround the metal. This glow gave a very brilliant spectrum. The spark from silver poles in air was brought into the same field of view as the vacuum glow, by means of a right-angled prism attached to the spectroscopic, and the two spectra were compared. The two strong green lines of silver were visible in each spectrum; the measurements taken of their wave-lengths were 3344 and 3675, numbers which are so close to Thalen's numbers as to leave no doubt that they are the silver lines. At a pressure giving a dark space of 2 m.m. the spectrum was very bright, and consisted chiefly of the two green lines and the red and green hydrogen lines. The intercalation of a Leyden jar into the circuit does not materially increase the brilliancy of the lines, but it brings out the well-known air lines. At this pressure not much silver flies off from the pole. At a higher vacuum the luminosity round the silver pole gets less and the green lines vanish. At an exhaustion of about one-millionth of an atmosphere the luminosity is feeble, the silver pole has exactly the appearance of being red hot, and the volatilisation of the metal proceeds rapidly.*

If, for the negative electrode, instead of a pure metal such as cadmium or silver, an alloy was used, the different components might be shot off to different distances, and in this way make an electrical separation—a sort of fractional distillation. A negative terminal was formed of clean brass, and submitted to the electrical discharge *in vacuo*; the deposit obtained was of the colour of brass throughout, and on treating the deposit chemically I

* Like the action producing volatilisation, the "red heat" is confined to the superficial layers of molecules only. The metal instantly assumes, or loses, the appearance of red heat the moment the current is turned on or off, showing that, if the appearance is really one to a rise of temperature, it does not penetrate much below the surface. The extra activity of the metallic molecules necessary to volatilise them is, in these experiments, confined to the surface only, or the whole mass would evaporate at once, as when a metallic wire is degraded by the discharge of a powerful Leyden jar. When this extra activity is produced by artificial heat one of the effects is the emission of red light; so it is not unreasonable to imagine that when the extra activity is produced by electricity the emission of red light should also accompany the separation of molecules from the mass. In comparison with electricity, heat is a wasteful agent for promoting volatilisation, as the whole mass must be raised to the requisite temperature to produce a surface action merely; whereas the action of electrification does not appear to penetrate much below the surface.

could detect no separation of its component metals, copper and zinc.

A remarkable alloy of gold and aluminium, of a rich purple colour, has been kindly sent me by Prof. Roberts-Austen. Gold being very volatile in the vacuum tube, and aluminium almost fixed, this alloy was likely to give different results from those yielded by brass, where both constituents fly off with almost equal readiness. The Au-Al alloy had been cast in a clay tube, in the form of a rod 2 c.m. long and about 2 m.m. in diameter. It was sealed in a vacuum tube as the negative pole, an aluminium pole being at the other side. Part of the alloy, where it joined the platinum wire passing through the glass, was closely surrounded with a narrow glass tube. A clean glass plate was supported about 3 m.m. from the rod of alloy. After good exhaustion the induction current was passed, the alloy being kept negative. Volatilisation was very slight, but at the end of half an hour a faint purple deposit was seen both on the glass plate and on the walls of the tube. On removing the rod from the apparatus it was seen that the portion which had been covered by the small glass tube retained its original purple appearance, while the part that had been exposed to electrical action had changed to the dull white colour of aluminium. Examined under the microscope, the whitened surface of the Austen alloy was seen to be pitted irregularly, with no trace of crystalline appearance.

This experiment shows that, from an alloy of gold and aluminium, the gold is the first to volatilise under electrical influence, the aluminium being left behind. The purple colour of the deposit on glass is probably due to finely-divided metallic gold. The first deposit from a negative pole of pure gold is pink; this changes to purple as the thickness increases. The purple then turns to green, which gets darker and darker until the metallic lustre of polished gold appears.

Returning to the analogy of liquid evaporation, if we take several liquids of different boiling-points, put them under the same pressure, and apply the same amount of heat to each, the quantity passing from the liquid to the gaseous state will differ widely in each case.

It was interesting to try a parallel experiment with metals, to find their comparative volatility under the same conditions of temperature, pressure, and electrical influence. It was necessary to fix upon one metal as a standard of comparison, and for this purpose I selected gold, its electrical volatility being great, and it being easy to prepare in a pure state.

An apparatus was made that was practically a vacuum tube with four negative poles at one end and one positive pole at the other. By a revolving commutator I was able to make electrical connection with each of the four negative poles in succession for exactly the same length of time (about six seconds); by this means the variations in the strength of the current, the experiment lasting some hours, affected each metal alike.

The exposed surface of the various metals used as negative poles was kept uniform by taking them in the form of wires that had all been drawn through the same standard hole in the drawplate, and cutting them by gauge to a uniform length; the actual size used was 0.8 m.m. in diameter and 20 m.m. long.

The comparison metal gold had to be used in each experiment; the apparatus thus enabled me to compare three different metals each time. The length of time that the current was kept on the revolving commutator in each experiment was eight hours, making two hours of electrification for each of the four negative electrodes; the pressure was such as to give a dark space of 6 m.m.

The fusible metals, tin, cadmium, and lead, when put into the apparatus in the form of wires, very quickly melted. To avoid this difficulty a special form of pole was devised. Some small circular porcelain basins were made, 9 m.m. diameter; through a small hole in the bottom a short length of iron wire, 0.8 m.m. in diameter, was passed, projecting downwards about 5 m.m.; the

basin was then filled to the brim with the metal to be tested, and was fitted into the apparatus exactly in the same way as the wires; the internal diameter of the basins at the brim was 7 m.m., and the negative metal filed flat was thus formed of a circular disc 7 m.m. diameter. The standard gold pole being treated in the same way, the numbers obtained for the fusible metals can be compared with gold, and take their place in the table.

The following table of the comparative volatilities was in this way obtained, taking gold as = 100:—

Palladium	108.00
Gold	100.00
Silver	82.68
Lead	75.04
Tin	56.96
Brass	51.58
Platinum	44.00
Copper	40.24
Cadmium	31.99
Nickel	10.99
Iridium	10.49
Iron	5.50

In this experiment equal surfaces of each metal were exposed to the current. By dividing the numbers so obtained by the specific gravity of the metal, the following order is found:—

Palladium	9.00
Silver	7.88
Tin	7.76
Lead	6.61
Gold	5.18
Cadmium	3.72
Copper	2.52
Platinum	2.02
Nickel	1.29
Iron	0.71
Iridium	0.47

Aluminium and magnesium appear to be practically non-volatile under these circumstances.

The order of metals in the table shows at once that the electrical volatility in the solid state does not correspond with the order of melting-points, of atomic weights, or of any other well-known constant. The experiment with some of the typical metals was repeated, and the numbers obtained did not vary materially from those given above, showing that the order is not likely to be far wrong.

It is seen in the above table that the electrical volatility of silver is high, while that of cadmium is low. In the two earlier experiments, where cadmium and silver were taken, the cadmium negative electrode in 30 minutes lost 7.52 grs., whilst the silver negative electrode in 1½ hours only lost 0.19 gr. This apparent discrepancy is easily explained by the fact (already noted in the case of cadmium) that the maximum evaporation effect, due to electrical disturbance, takes place when the metal is at or near the point of liquefaction. If it were possible to form a negative pole *in vacuo* of molten silver, then the quantity volatilised in a given time would be probably much more than that of cadmium.

Gold having proved to be readily volatile under the electric current, an experiment was tried with a view to producing a larger quantity of the volatilised metal. A tube was made having at one end a negative pole composed of a weighed brush of fine wires of pure gold, and an aluminium pole at the other end.

The tube was exhausted and the current from the induction coil put on, making the gold brush negative; the resistance of the tube was found to increase considerably as the walls became coated with metal, so much so that, to enable the current to pass through, air had to be let in after a while, depressing the gauge ½ m.m.

The weight of the brush before experiment was

35.4940 grs. The induction current was kept on the tube for 14½ hours; at the end of this time the tube was opened and the brush removed. It now weighed 32.5613, showing a loss of 2.9327 grs. When heated below redness the deposited film of gold was easily removed from the walls of the tube in the form of very brilliant foil.

After having been subjected to electrical volatilisation, the appearance of the residual piece of gold under the microscope, using a ¼-inch object-glass, was very like that of electrolytically deposited metal, pitted all over with minute hollows.

This experiment on the volatilisation of gold having produced good coherent films of that metal, a similar experiment was tried, using a brush of platinum as a negative electrode. On referring to the table it will be seen that the electrical volatility of platinum is much lower than that of gold, but it was thought that by taking longer time a sufficient quantity might be volatilised to enable it to be removed from the tube.

The vacuum tube was exhausted to such a point as to give a dark space of 6 m.m., and it was found, as in the case of gold; that as a coating of metal was deposited upon the glass the resistance rapidly increased, but in a much more marked degree, the residual gas in the tube apparently becoming absorbed as the deposition proceeded. It was necessary to let a little air into the tube about every 30 minutes, to reduce the vacuum. This appears to show that the platinum was being deposited in a porous spongy form, with great power of occluding the residual gas.

Heating the tube when it had become this way non-conducting liberated sufficient gas to depress the gauge of the pump 1 m.m., and to reduce the vacuum so as to give a dark space of about 3 m.m. This gas was not re-absorbed on cooling, but on passing the current for ten minutes the tube again refused to conduct, owing to absorption. The tube was again heated, with another liberation of gas, but much less than before, and this time the whole was re-absorbed on cooling.

The current was kept on this tube for 25 hours; it was then opened, but I could not remove the deposited metal except in small pieces, as it was brittle and porous. Weighing the brush that had formed the negative pole gave the following results:—

Weight of platinum before experiment ..	10.1940	Grains.
" " after experiment ..	8.1570	
Loss by volatilisation in 25 hours	2.0370	

Another experiment was made similar to that with gold and platinum, but using silver as the negative pole, the pure metal being formed into a brush of fine wires. Less gas was occluded during the progress of this experiment than in the case of platinum. The silver behaved the same as gold, the metal deposited freely, and the vacuum was easily kept at a dark space of 6 m.m. by the very occasional admission of a trace of air. In 20 hours nearly 3 grs. of silver were volatilised. The deposit of silver was detached without difficulty from the glass in the form of brilliant foil.

A NOVEL METHOD FOR THE PRODUCTION OF SODIUM AND POTASSIUM NITRITE.

By H. N. WARREN, Research Analyst.

THE surface, or catalytic action, which platinum exerts upon ammonia when in the presence of oxygen, with the production of the white cloud of ammonium nitrite, is, when carefully performed, more than striking as regards the quantity of nitrite thus formed, but by employing a more energetic form of platinum the effects may be considerably enhanced.

The most powerful surface action that I have been

successful in producing was obtained as follows:—Platinum was dissolved by the aid of aqua regia, evaporated to dryness, and the resulting platinum chloride thus formed maintained at a temperature of 400° F. as long as any chlorine continued to be evolved; the residue was now boiled with a slight excess of sodium carbonate, and the platinum hydrate thus produced dissolved by means of oxalic acid, the solution concentrated, and a sufficiency of asbestos yarn added to absorb the solution; the yarn, which now measured about a yard in length, when dried and ignited contained about 12 per cent of platinum, presenting a grey colour characteristic of that metal when in the spongy form, the asbestos meanwhile retaining its original ropy properties without becoming brittle, as is the case when platinum chloride is used in place of the oxalate. The so-prepared asbestos was next introduced into a combustion-tube somewhat longer than the same, and connected to an apparatus evolving ammonia gas: a current of air being at the same time injected into the apparatus, in order to furnish a mixture of oxygen and ammonia, the action of the platinumised asbestos was now started by applying the flame of a Bunsen burner to the more remote end of the tube. Directly the mixed gases are allowed to impinge upon the platinumised surface, dense clouds of ammonium nitrite are evolved, and in several instances the whole length of the asbestos became intensely heated, the ammonium nitrite thus formed being conveyed into a solution of caustic soda, and, by so doing, producing an equivalent of sodium nitrite; the ammonia thus evolved being retained for a further supply of ammonium nitrite.

Some idea as to the delicacy of this so-prepared asbestos can be obtained when I mention that for several minutes, while the apparatus was in complete working order, scarcely any excess of ammonia could be detected at the further end of the tube, the whole of it being converted into that of nitrite.

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ASSOCIATION VERSUS DISSOCIATION IN SOLUTIONS.*

By SPENCER UMPREVILLE PICKERING, M.A., F.R.S.

THE view that electrolytes in aqueous solutions are partially dissociated into their ions is chiefly based on the correctness of the evidence as to the number of molecules or acting units present afforded by the depression of the freezing-point of the solvent. If this method is reliable, it will afford consistent evidence in whatever way it may be applied.

When $5\text{H}_2\text{SO}_4$, for instance, are dissolved in $15\text{H}_2\text{O}$, some of the acid molecules become dissociated according to the modern physical theory of solution, so that the solution consists of *more than* twenty acting units; according to the hydrate theory, on the other hand, the acid and water combine together to a certain extent, so that the solution consists of *less than* twenty acting units. By adding this solution to some other crystallisable liquid, such as acetic acid, we can, according to the physical theory, determine the number of acting units of which it is composed; and the result shows that, instead of consisting of more than twenty acting units, it consists of only 6.5 units. Thus the very phenomenon on which the physical theory is based gives most emphatic evidence against that theory.

The sulphuric acid and water together produce a smaller depression of the freezing-point of acetic acid than the water alone does, so that on adding sulphuric acid to dilute acetic acid, the freezing-point of the latter is actually raised. A series of determinations was made

* Abstract of a Paper read before the German Chemical Society.

In which different amounts of sulphuric acid were added to weak acetic acid, and the results gave the data requisite for the construction of the following table, in which the depression actually produced by the water and sulphuric acid is compared with that which would be produced if these two acted independently.* In the extreme case the observed depression amounts to only one-third of the calculated value.

Molecules to 100 $C_2H_3O_2 = x$.	Depression for $14'4 H_2O + (x-14'4)H_2SO_4$.		
	Calculated.	Found.	Difference.
14'4	—	—	—
15'0	6'76°	5'65°	- 1'11° = 16 p.c.
17'5	8'00	3'77	- 4'23 = 53 "
20	9'08	2'95	- 6'13 = 68 "
25	12'53	3'45	- 9'08 = 72 "
30	17'09	6'00	- 11'09 = 65 "
35	24'70	9'65	- 15'05 = 61 "
40	∞	14'00	∞
45	∞	19'15	∞
50	∞	26'00	∞
55	∞	39'50	∞

In these determinations the minimum proportion of sulphuric acid to water corresponded to that of a 40 per cent solution, and such a solution is held to behave anomalously, owing to its strength being too great for the correct application of Van t' Hoff's theory of the lowering of the freezing-point. On plotting out all the results, however, it was evident that the phenomenon which they exhibited would also be exhibited by solutions containing a far smaller proportion of sulphuric acid; but to remove all doubt that this was the case, the following determinations were made:—

Water +	Molecules of Sulphuric acid To 100 ($C_2H_3O_2$).	Total	Depression.
16'8	+ 0	= 16'8	7'32°
16'8	+ 0'017	= 16'827	7'23
16'8	+ 0'035	= 16'835	7'18
16'8	+ 0'054	= 16'854	7'16
16'8	+ 0'097	= 16'897	7'03

In the second and third of these determinations the sulphuric acid and water form solutions containing only 0'1 and 0'6 per cent of the former respectively, and such solutions, Arrhenius maintains (CHEM. NEWS, lxiii., 148), behave in strict accordance with the dissociation and osmotic pressure theories. Each molecule of acid becomes, according to him, dissociated into 2'14 ions (on the average), forming, that is, 1'14 more acting units than were present before the dissolution. Yet the present determinations show that this is not the case; the number of acting units is diminished by 0'21 and 0'32 in the two cases, instead of being increased by 1'14.

Other substances which possess a strong affinity for water behave like sulphuric acid, and actually raise the freezing-point of weak acetic acid. This was found to be the case with hydrochloric acid to a very marked extent, and in a smaller degree with calcium chloride. With phosphoric acid there was no raising of the freezing-point of weak acetic acid of the strength which was taken, but the additional lowering produced was almost nil—that is, the water and phosphoric acid caused a depression scarcely in excess of that caused by the water only. With nitric acid the additional depression was considerable, but yet it was notably smaller than that which would be produced if no combination between the water and acid had occurred.

It must be remarked that, according to the hydrate theory, the present results will not afford any indication of the actual hydrates present. When sulphuric acid, for instance, is dissolved in water, the present hydrate theory

represents the whole liquid (unless excessively dilute) to consist of one or more hydrates. When this liquid is cooled, the water molecules which coalesce to form solid water are derived from these hydrates, the latter becoming decomposed into other hydrates containing less water and the only portion of the liquid which acts as the "foreign substance" is that from which none of the solvent can be separated by cooling, that is, the sulphuric acid, and not the hydrate. It is the mechanical or physical effect of these "foreign" molecules to which the lowering of the freezing-point of the solvent must be mainly attributed in the case of dilute solutions, for the chemical union of the acid and water can have but a small effect on the result, since the heat absorbed by the decomposition of a high hydrate into that next below it is very small in comparison with the heat evolved by the crystallisation of the water which it gives up (see *Proc. Chem. Soc.*, 1889, p. 149). When there are two dissolved substances present, the results will be very complicated; the acetic acid and the sulphuric acid, for instance, will each combine with some water in proportions dependent on their relative affinities for water and on the masses of each present, and the molecules acting as "foreign" molecules and causing the depression will be those water molecules which are combined by the acetic acid (the solvent) and the molecules of the hydrate of sulphuric acid. The case is evidently too complicated for any deductions to be drawn as to the composition of the latter.

In a case where the substance added to the acetic acid and water has a much smaller affinity for the water than the acetic acid has, this latter will appropriate nearly the whole of the water, and the other substance will remain almost anhydrous, or will itself combine with the acetic acid to form compounds analogous to hydrates. In such a case the whole of the water (being combined with the solvent itself), as well as the other substance, will act as the "foreign substance."

This was found to be the case with alcohol when added to acetic acid containing water, the depression of the freezing-point observed being practically identical with that which is produced by the alcohol and water when acting separately. The same was also the case when water and acetic acid were added to sulphuric acid as a solvent, the latter, as might have been expected, taking practically the whole of the water, and the acetic acid none.

Other results were obtained with calcium chloride and alcohol, and also with calcium nitrate and alcohol, dissolved in water. These two salts, which both possess a considerable affinity for alcohol, appear to combine with it, and depress the freezing-point of water to a smaller extent than that calculated on the assumption that they and the alcohol act independently; but the diminution of the depression was not large unless the proportion of salt added was considerable.

The only conclusion which can be drawn from these results is that when two substances possessing a strong affinity for each other are mixed, there are fewer acting units present than when they are separate, and that, therefore, these two substances do not interact so as to produce dissociation, but combination.

ON THE USE OF AMMONIUM SELENITE FOR THE DIAGNOSIS OF THE ALKALOIDS.

By A. J. FERREIRA DA SILVA.

In a note presented to the Academy in June, 1885, Lafon pointed out a new reagent for morphine and codeine. It is ammonium sulphoselenite, which he prepared by dissolving 1 grm. ammonium selenite in 20 c.c. of undiluted sulphuric acid. This reaction gives a green colour with

* For the exact method of calculation the present number of the *Berichte* must be consulted.

the two alkaloids mentioned, but others behave in a different manner. It is a precious reagent in the toxicological study of poisoning cases by the alkaloids of opium.

The author finds that its use may be advantageously extended for the detection of some other alkaloids.

He has operated upon the following alkaloids: atropine, aconitine, berberine, brucine, caffeine, cinchonine, cinchonidine, cocaine, curarine, delphine, digitaline, eserine, morphine, narcotine, narceine, papaverine, pilocarpine, solanine, saponine, senegine, and veratrine. The following results were obtained:—

Atropine.—No colouration.

Aconitine.—No immediate colouration; after twenty minutes a very slight rose-colour.

Berberine.—Greenish yellow colour, becoming successively very brown, rose at the margins, and violet in the middle; half-an-hour afterwards entirely vinous red, which lasts for three hours.

Brucine.—Reddish or rose-colour, becoming pale orange. Half-an-hour after an amber colour, and no deposit.

Caffeine.—No distinct colouration. At the end of three hours the liquid was reddish, and there appeared a very slight deposit, which was not red.

Cinchonine.—Nothing.

Cinchonidine.—Nothing.

Cocaine.—After half-an-hour no decided colouration nor precipitate. After the lapse of three hours the same reaction as caffeine.

Curarine.—Slight violet colouration, after some time reddish. No red deposit at the end of three hours.

Delphine.—Slightly reddish colouration passing into a violet red. No precipitate at the end of three hours.

Digitaline.—No immediate colour. Half-an-hour after the liquid was yellowish. After three hours a reddish deposit.

Eserine.—Lemon-yellow colour, turning to orange. Three hours afterwards the colour paler.

Morphine.—Bright greenish blue; half-an-hour after maroon-yellow and no deposit. After three hours the liquid maroon-brown; no red deposit.

Narcotine.—Bluish colour, becoming violet and then reddish. After half-an-hour a fine reddish colour and no precipitate. After three hours a small red deposit.

Narceine.—Yellow-green colour, becoming brownish, and after half-an-hour reddish. Afterwards a red deposit at the bottom of the capsule, which is very distinct in two or three hours.

Papaverine.—Bluish colour; the liquid becomes bottle-green, dirty yellowish green, violet-blue, and then red. A small bluish deposit at the bottom of the capsule.

Pilocarpine.—Nothing.

Solanine.—Canary-yellow, and then brownish. After half-an-hour a rose-coloured ring. After three hours the liquid violet-red.

Saponine.—Yellowish, becoming slightly reddish. (Reaction not distinct).

Senegine.—Light dirty yellow. After three hours liquid reddish.

Veratrine.—Indistinct yellowish colour, sometimes with a green tone, after half-an-hour yellow. After three hours' deposit red and liquid yellowish. (Reaction indistinct).

Lafon's reagent thus enables us to distinguish not only morphine and codeine, but also berberine, eserine, narcotine, papaverine, solanine, and narceine; the former by colour reactions; narceine not only by the immediate production of a yellowish green colour passing into brown and after half-an-hour to reddish, but also by the formation of a red deposit, which is seen more distinctly after the lapse of two or three hours adhering to the sides, and the bottom of the capsule.

The author in producing these reactions places small portions of the alkaloids upon watch-glasses set upon

white paper, or in small porcelain capsules (3 c.m. in diameter and 4 c.c. in capacity).—*Comptes Rendus*, vol. cxii., p. 1266.

DETECTION AND SEPARATION OF THE PLATINUM METALS, AND IN PARTICULAR OF PALLADIUM AND RHODIUM, IN PRESENCE OF THE COMMON METALS.

By A. JOLY and E. LEIDIE.

WHEN the platinum metals are united with large quantities of common metals, such as copper, iron, lead, bismuth, and tin, great difficulty is experienced in the detection of their presence and in their accurate separation. The studies which the authors have undertaken during the last two years on the combination formed by some of the metals of native platinum with nitrous acid, and the alkaline nitrites taken together, with facts previously observed by Fischer and Lang (palladio-nitrites, platino-nitrites), by Claus and W. Gibbs, enable this separation to be effected in most cases.

We first exclude osmium, ruthenium, and iridium. We admit, for instance, that the platinum ores have first been treated by the method of Deville and Debray, that the osmium and ruthenium have been eliminated in the state of volatile compounds, and that the iridium has been separated by means of lead. The residues from these operations will have left in a solution which we will suppose to be hydrochloric small quantities of platinum, palladium, and rhodium, with common metals such as lead, iron, copper, bismuth, tin, &c., which pre-existed in the ore, or which may have been introduced as impurities in the considerable quantities of lead which have to be used.

The reactions exerted by potassium nitrite upon the hydrochloric solutions of the metals just mentioned are perfectly definite.

The progressive addition of potassium nitrite to a solution of palladium chloride kept luke-warm, occasions the progressive decolouration of the liquid, and when this becomes neutral it takes a characteristic gold-colour, and after concentration it deposits crystals of palladio-nitrite, which are sparingly soluble in the cold, especially in presence of an excess of alkaline chlorides.

Platinum is transformed under the same conditions as palladium into a colourless platino-nitrite. It is here necessary that the potassium chloroplatinate which is necessarily formed at first shall not be deposited, and this requires that the chief part of the platinum must be previously eliminated, or that the liquid is sufficiently diluted.

In a hot and dilute solution of rhodium chloride potassium nitrite determines the formation of a white, crystalline precipitate of double nitrite, insoluble in a solution of potassium chloride. It is to be remarked that the precipitation of the double salt takes place when the liquid is still acid.

If the hydrochloric solution contains lead this is precipitated in a slightly acid liquid along with the bismuth and the tin. The precipitation of the copper begins in an acid liquid, and is completed not until the moment when the liquid becomes distinctly alkaline. The presence of copper is shown on the first additions of nitrite by an intense green colouration. A bluish-white flocculent precipitate is then formed, which is gradually changed into a granular precipitate of a light blue. As for the iron it is only eliminated in the last place in the alkaline liquid in the form of a gelatinous brown precipitate, very soluble in dilute hydrochloric acid.

Suppose a hydrochloric solution of the above metals. To this solution suitably diluted (as may be found by trial on a small portion), and kept at 60°, potassium

nitrite is progressively added. If the liquid is rich in platinum there is gradually formed a crystalline precipitate of the chloro-salt, perfectly free from the other metals. After cooling and separation of the chloro-salt it is heated again, and the additions of nitrite are continued. There is suddenly formed, especially on rubbing with a glass rod, the crystalline double rhodium precipitate, which carries down with it lead, bismuth, and tin.

This double salt is analogous in its composition to the double potassium and cobalt nitrite, and seems to behave like the latter. That is it which forms triple combinations containing lead and bismuth. The precipitate of rhodium is slightly cupriforous. At this point the liquid is still acid; it is allowed to cool to separate the rhodium salt, the precipitation of which is in general complete if the liquid contains a sufficiency of potassium chloride. If the mixture contains copper and iron more nitrite is added to render the liquid alkaline, and it is heated to ebullition. Iron and copper are filtered off, whilst the platinum and palladium are entirely present in the solution, which is of a gold colour. If the platinum and palladium are in considerable quantities the double nitrites are crystallised out. Otherwise the salts are transformed into chlorides by dilute hydrochloric acid and eliminated by known methods.—*Comptes Rendus*, vol. cxii., p. 1259.

SEPARATION AND DETERMINATION OF NICKEL AND COBALT.

By CONSTANTIN KRAUSS.

(Concluded from p. 281).

C.—Methods depending on the Different Behaviour of the Phosphates of Both Metals.

1. Ph. Dirvell separates cobalt and nickel (from accompanying metals) in the known manner, and determines the sum of both by weighing the metals reduced in a current of hydrogen. For further separation he re-dissolves the metals in nitric acid, evaporates down the solution, and re-dissolves in 50 c.c. water.

So much of a phosphatic solution (mixed with an equal volume of a solution of ammonium carbonate), that thirty times as much phosphate is present as the joint weight of the cobalt and nickel. The mixture is now slowly heated, boiled for a few seconds, and mixed with 2–3 c.c. ammonia, when the chief part of the precipitate formed is re-dissolved. If it is now cautiously heated to 100° we obtain a purple-violet precipitate, which when filtered, washed, and ignited, corresponds to the formula $\text{Co}_2\text{P}_2\text{O}_7$. The nickel is thrown down from the filtrate by means of sulphuretted hydrogen and determined in the known manner.

According to Krauss this method, after some experience, yields satisfactory results. The liquid must be frequently agitated, especially after the addition of the ammonia, and the ebullition must not be continued too long. The cobalt obtained generally contains nickel. The clear solution is then decanted off, the precipitate dissolved in a little phosphoric acid, and re-precipitated as before.

The separation of the nickel in the filtrate and its determination as nickel sulphide cannot be recommended, as it has no constant composition and is not insoluble in the ammoniacal solution. According to Krauss it is preferable to treat the ammoniacal solution of nickel with potassa-lye in excess, to boil until all the ammonia has escaped, and to precipitate with bromine water.

Pisani's proposed modification—the use of ammonium acetate in place of ammonium carbonate—cannot be regarded as an improvement.

J. Clark's modification of the Dirvell process (*CHEMICAL NEWS*, vol. xlviii., p. 262), is not considered by Krauss as in any manner an improvement.

D.—Methods of Separation and Determination on Various Principles.

1. N. W. Fischer's proposed separation of cobalt and nickel in an acetic solution by means of potassium nitrite has been already carefully studied by Fr. Gauhe and others and recommended as excellent (*Poggendorff's Annalen*, vol. lxxii., p. 474, and *Zeit. Anal. Chem.*, vol. v., p. 74).

2. Demarçay proposes to use for the separation of the two metals the behaviour of the ammoniacal solution of their salts with metallic zinc.

The experiments undertaken by Krauss show that nickel is first precipitated by metallic zinc, but that we have no certain indication when all the nickel is precipitated and the cobalt begins to fall. Demarçay, in his original communication, states that the cobalt is deposited first (*Bull. de la Soc. Chimique de Paris*, vol. xxxii, p. 610).

3. W. Skey proposes a method in the *CHEMICAL NEWS*, vol. xvi., p. 202, which Krauss finds unsatisfactory.

4. F. W. Clarke (*CHEMICAL NEWS*, vol. xx., p. 154), utilises the ready solubility of nickel ferricyanide in ammonia. The separation is approximately quantitative, but the quantity of nickel is generally found deficient. Further, after the destruction of the ferricyanides, it is necessary to separate these metals from iron.

5. W. Gibbs proposes to precipitate the nickel or cobalt salts with oxalic acid, to filter off the precipitate, and to titrate the excess of oxalic acid in the filtrate. This method was found especially inaccurate, as the metallic oxalates are somewhat soluble. Better results are obtained if, according to A. Classen, we precipitate the nickel as oxalate by adding acetic acid to a solution of potassium nickel oxalate, dissolve the precipitate in hydrochloric acid, heat to 50°, and titrate with permanganate. In this case it is certainly simpler to ignite the nickel oxalate and to weigh the resulting nickelous oxide.

6. M. Ilinski and G. von Knorre (*Berichte Deutsch. Chem. Gesell.*, vol. xviii., p. 699), mixed the solution of the two metals with a few c.c. of hydrochloric acid, and added to the hot liquid a hot solution of a sufficiency of nitroso- β -naphthol in acetic acid of 50 per cent. After some hours the precipitate of cobaltinitroso- β -naphthol is filtered off, washed with 12 per cent hydrochloric acid, first cold and then hot, and lastly with hot water. The dried precipitate, along with the burnt filter and a few knife-points full of pure oxalic acid, are placed in a Rose's crucible, and after incineration the metal is determined by ignition in a current of hydrogen. The nickel is found by determining the joint weight of nickel and cobalt in an aliquot part of the original substance or calculating the nickel from the difference; or the filtrate obtained on separating the cobalt is evaporated to dryness, ignited, dissolved in hydrochloric acid and a few drops of nitric acid, and the nickel is determined by precipitation with potassa-lye.

According to the experiments of Krauss very good results are obtained by this process. The quantity of cobalt operated upon must not be too large, and care must be taken that it is entirely precipitated. A relatively very large proportion of nitroso- β -naphthol solution is required for this purpose, and the precipitate formed is very bulky.

The reaction with cobalt and nitroso- β -naphthol is so sensitive that a visible turbidity is occasioned by traces which cannot be distinguished by the nitrite reaction. An ignition of the precipitate with oxalic acid, or preferably in a feeble current of oxygen, is necessary, especially for large quantities of cobalt. If this precaution is omitted the results are always too high. The cobalt seems to form a compound with carbon which is not destroyed even by ignition ever the blast. If a considerable quantity of cobaltinitroso- β naphthol is ignited first over an open flame and then over the blast until there is no more emission of light from burning organic matter,

and the mass glows with a uniform dark red, there is obtained a heavy black powder. If this is covered with cold hydrochloric acid there are formed a black residue and a solution of cobalt chloride of an intense violet colour, which, on evaporation, leaves a gelatinous mass. This can be destroyed by renewed ignition, whilst the black residue is incombustible. If the latter is treated with *aqua regia* at a boiling heat there is obtained a reddish brown or dark brown liquid, which becomes of an intense green on evaporation. From this solution cobalt carbonate is precipitated by sodium carbonate. If this is filtered off and the alkaline filtrate mixed with bromine water there is a further precipitation of cobalt oxide, and even in the filtrate from this precipitate cobalt can still be demonstrated after concentration and ignition.

The author refers, in conclusion, to the new element which Krüss and F. W. Schmidt have found accompanying cobalt and nickel. He expresses the conjecture that a variety of phenomena which he encountered during his researches may be explained by the presence of this element, such as the difficulty of obtaining sulphides of uniform composition, and above all, the fluctuating composition of the oxides, which render their iodometric determination almost impossible.—*Zeit. Anal. Chemis.*, vol. xxx., p. 327—242.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

Method and Reactions of the Various Elements.

THIS condensed communication of micro-chemical manipulations and reactions is intended, as far as possible, to transplant the microscope from the workroom of the petrographist to the laboratory of the analytical chemist. The previous reluctance of chemists to take up these methods seems to me to have a twofold ground—on the one hand, in the belief that a tedious training in the use of the microscope is an indispensable preliminary, and, on the other, in the incompleteness and the unsuitable selection of the micro-chemical reactions which have hitherto been made known. To the former part I will return in the sequel. As regards the second I will state the points of view which I have considered decisive in the choice of reactions, and which must be decisive in future if the microscope is to become naturalised in chemical laboratories.

1. *Minimum Expenditure of Material.*—In order to be able to work with hundredths of a milligramme, in certain cases (*e.g.*, Cl, Pt, Ti, Mg) with millionths of a milligramme the reactions must be exceedingly sensitive. This depends not merely on the sparing solubility of the compounds to be produced, but on their molecular volumes, and quite as much on their ability to form larger crystals. For instance, under the microscope the reaction for silver by the formation of the chromate is quite as sensitive as that by formation of the much less soluble chloride, simply from the reason that the crystals of the chromate are about 100 times as large as those of the chloride. Intense colouration plays a subordinate part. If we have to do with powdery precipitates or coloured liquids, the colouration can scarcely be recognised under high magnifying power.

2. *Minimum Expenditure of Time.*—I felt tempted to give this condition the first place, since the extension of the micro-chemical method depends on it more than all others. That it is practicable, by means of micro-chemical reactions, to submit granules of 0.1 m.m. in diameter to a qualitative examination, is very important for the petrographer, and the chief weight has been laid upon it. Hence micro-chemical analysis, from its origin

down to the present day, has remained almost exclusively in the hands of the petrographers. Chemists will feel much more interest in learning that, by the aid of chemical reactions, many investigations may be considerably abridged, and that even greater economy of time is probable on a further development of the method. The detection of the metals in a solution containing calcium, magnesium, zinc, manganese, cobalt, and nickel (about $\frac{1}{2}$ m.grm. of each), was completed in 40 minutes. In another case, where silver, mercury, lead, bismuth, tin, antimony, and arsenic were present, the complete detection was effected within an hour. It is practicable to carry out the investigation on a single object slip of the ordinary long form, so that all the final products were disposed within this small space, which under some circumstances may be very convenient.

In order to economise time and room, reactions which require circumstantial preparation must be excluded, as also such as are tedious in execution. Thus Haushofer's proposed test for glucinum as a chloroplatinate must be rejected, because the crystallisation can be produced only with the aid of the exsiccator. The precipitation of zirconium oxide with potassium sulphate is excluded, since it often does not commence before the lapse of half an hour. The separation of cobalt and nickel by means of oxalic acid and ammonia, which has again been proposed for micro-chemical use by Haushofer, must be decidedly rejected, as it may take longer than half a day. Filtration is admissible only in cases where there is no other expedient. This cuts off many reactions otherwise suitable, as they can be carried out only in a clear liquid. Sparingly soluble compounds which crystallise well and readily best meet this condition, and are most suitable for micro-chemical reactions.

3. *Trustworthiness of the Reactions.*—The reactions must take place with certainty; they must be perceived without difficulty, and they must be characteristic. A reaction which is affected by a slight change in temperature, or in the composition of the solvent, must be at once renounced. It is not possible to work under such conditions when we have to deal at the outside with centigrammes. The number of reactions of general applicability is unpleasantly limited by changes in the form of the characteristic compounds which occur in presence of a third or fourth element. Such reactions may be characteristic in simple solutions, whilst in mixed solutions they may be useless. Cadmium and zinc, when each occurs alone, may be distinguished by means of their oxalates. If they occur together in the same solution the zinc may be recognised by means of oxalic acid, but not the cadmium. Calcium tartrate and calcium carbonate crystallise easily from solutions which contain no barium. If the latter is present neither of the metals can be recognised in the pulverulent or spherulitic precipitates.

In order that the reactions may be distinct, which is desirable not alone for the sake of accuracy but for the speedy completion of a research, the characteristic crystals must not be so minute that it is necessary to use a magnifying power of 400 or 600 diameters. Especially in this most unfavourable case there should not be formed large masses of pulverulent or flocky by-products, among which the crystals may lie hid, as, for instance, the tiny crystals of zirconium oxide obtained by fusion with sodium carbonate (Lévy and Bourgeois) along with a large excess of pulverulent and granular matter.

(To be continued).

Apparatus for the Reduction of Gaseous Volumes to Normal Temperature and Pressure.—Prof. Lunge.—The author's apparatus, which should have been figured, gives the volume of a gas reduced to 0° and to a pressure of 760 m.m. (*Zeit. Angewandte Chemie*).—*Monsieur Scientifique Queneville*, Vol. iv., Part 2.

* *Zeit. Anal. Chemis.*

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

May 21st, 1891.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

Messrs. J. A. Foster, William MacDonald, and F. H. Moore were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick R. Holloman, Sugar Refinery, Rawcliffe Bridge, Selby; Arthur Michael, Torwood, Boncharch, Isle of Wight; F. M. Perkin, Heriot Watt College, Edinburgh; Edmund Charles Rossiter, 39, Brook Green Road, Hammersmith; John Shields, The Byers, Bathgate, N.B.

The PRESIDENT announced that Dr. William Wegg had presented to the Society, through Mr. Warrington, a daguerreotype containing the portraits of Messrs. Brande, Cooper, and Phillips.

The following papers were read:—

20. "Bromo-derivatives of Betanaphthol." By HENRY E. ARMSTRONG and E. C. ROSSITER.

The authors have completed the study of the compounds formed on brominating betanaphthol, to which they have referred in two previous notices (*Proc. Chem. Soc.*, 1889, 71; 1890, 32). They give the following directions for the preparation of tri- and tetrabromobetanaphthol.

Tribromo-β-naphthol is prepared by adding somewhat more than three molecular proportions of bromine to betanaphthol dissolved in thrice its weight of acetic acid; the solution becomes hot, but must *not* be cooled. When all the bromine is added, the mixture is allowed to stand during one hour, and is then heated on the water-bath, at first gently, afterwards at 100°, as long as hydrogen bromide is evolved. The white solid product is recrystallised once or twice from acetic acid, and then

treated with twice the theoretical quantity of acetic chloride. The acetate is purified by crystallisation from acetic acid and benzene. When treated with alcoholic potash, it is easily converted into tribromonaphthol.

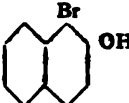
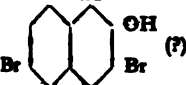
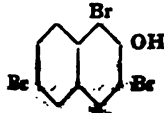
Tetrabromo-β-naphthol is prepared by adding somewhat more than four molecular proportions of bromine to betanaphthol mixed with an equal weight of acetic acid. The solution becomes very hot on adding the bromine, but must not be cooled. When all the bromine is added, the mixture is heated on the water-bath until it becomes quite solid. The product is purified by crystallising once or twice from acetic acid. It is then converted into the *acetate*, and this is crystallised from a mixture of benzene and acetic acid.

The properties of the bromobetanaphthols are summarised in the Table. The preparation of the bromo-betanaphthaquinones and of the α-nitrobromonaphthols, included in the fourth column of this table, is described in the next note.

The entire product of the action of bromine in excess on betanaphthol has been carefully examined without any substance having been discovered which affords 1:2:3-bromophthalic acid on oxidation; the explanation of the discrepancy between the author's observations and the earlier experiments of Smith and Meldola, therefore, yet remain to be discovered.

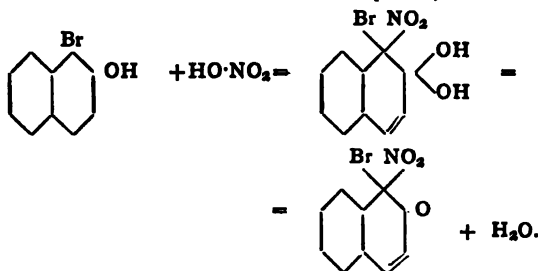
21. "The Action of Nitric Acid on Naphthol Derivatives as Indicative of the Manner in which Nitration is Effected in the case of Benzoid Compounds Generally. The Formation of Nitro-β-naphthols." By HENRY E. ARMSTRONG and E. C. ROSSITER.

When warmed with nitric acid, the chloro- and bromo-derivatives of betanaphthol are converted into derivatives of betanaphthaquinone, but, as the authors have pointed out in their previous notice, the formation of these products is preceded by that of an unstable intermediate compound. When these intermediate compounds are carefully heated, they are converted into bromo-derivatives of betanaphthaquinone, and in preparing these latter it is

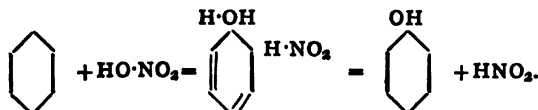
Bromo-derivative.	Description.	Acetate.	Convertible by HNO ₃ into
Monobromo-β-naphthol— 	Slender needles very soluble in acetic acid. M. p., 84°.	—	α ₁ -nitro-β-naphthol. M. p., 103°.
Dibromo-β-naphthol— 	Long shining needles moderately soluble in acetic acid. Crystallised with 1 molecular proportion of acetic acid, m. p., 84°. M. p., 106°.	Elongated lustrous plates. M. p., 125°.	{ C ₁₀ H ₇ BrO ₂ . M. p., 145°. C ₁₀ H ₆ Br ₂ O ₂ . M. p., 171°. α ₁ -nitrobrom-β-naphthol. M. p., 122°.
Tribromo-β-naphthol— 	Lustrous needles less soluble than the dibromo-compound. M. p., 155°.	Soft interlacing needles. M. p., 184°.	C ₁₀ H ₄ Br ₃ O ₂ . M. p., 150°. α ₁ -nitrodibrom-β-naphthol. M. p., 163°.
Tetrabromo-β-naphthol— 	Very slender silky needles sparingly soluble in acetic acid. M. p., 172°.	Short colourless prismatic needles. M. p., 189 to 190°.	C ₁₀ H ₃ Br ₄ O ₂ . M. p., 190°. α ₁ -nitrotetrabrom-β-naphthol darkens at 135°; melts at 136° with decomposition.

desirable to separate the intermediate compound from the excess of nitric acid, and to decompose it by carefully heating it with acetic acid, except in the case of tetrabromobetanaphthol; tribromobetanaphthaquinone is so readily formed from this compound, and is so difficultly soluble and well characterised, that small quantities of tetrabromobetanaphthol may be detected in presence of the di- and tri-bromo-derivatives by simply heating the mixture with acetic acid and nitric acid. Thus, if nitric acid be added to dibromobetanaphthol, suspended in acetic acid, a clear solution is obtained, which, after a short time, deposits a crystalline substance; if quickly separated by filtration, this product is almost colourless, but it decomposes when kept, becoming yellow. It was conceivable, judging from the manner in which it was produced, that the compound was a nitrate, formed by the simple displacement of the hydroxylic hydrogen by NO_2 , and the results of analysis were in accord with this view; but such a nitrate should be reconvertible into the parent substance by treatment with alkali, whereas actually it affords, as chief product, bromonitronaphthol. Bromobetanaphthol, in like manner, eventually yields α_1 -nitrobetanaphthol, and the tri- and tetrabromo-derivatives afford di- and tri-bromonitrobetanaphthol; the bromine atom displaced by NO_2 by this method of treatment, there can be little doubt, is invariably that in the α_1 -position.

The authors are of opinion that the intermediate compounds in question are nitrobromoketo-derivatives corresponding to the dichloroketo-compounds of Zincke, and that their formation affords evidence that the elements of nitric acid first become added to the bromonaphthol, thus—



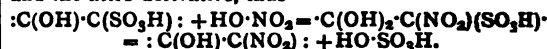
The theory that the formation of such addition compounds precedes that of nitro-compounds generally appears to afford a satisfactory explanation of a large number of well-known facts which hitherto have remained unexplained. The non-production of nitro-compounds from paraffins and their derivatives, except in a certain very limited number of special cases, appears as the natural consequence of the inability of paraffins to form addition compounds. The theory affords a simple explanation of the formation of nitro-derivatives of phenols on nitrating hydrocarbons, to which Nölting has drawn special attention in the case of toluene and orthoxylene (*Berichte*, 1885, 2670; 1888, 3158), for if the addition compound lose HNO_2 instead of $\text{H}\cdot\text{OH}$ a phenol would result, thus—



An agent that would favour the separation of the elements of water from the addition compound would increase the production of the nitro-compound and diminish that of the phenol; and, as a matter of fact, it is known that when a mixture of nitric and sulphuric acid is used there is less of the phenol derivative produced than when nitric acid alone is employed. A compound such as the addition compound of benzene with nitric acid above represented, would obviously be unstable and prone to undergo oxidation; hence it is not difficult to under-

stand that so large an amount of nitrous fume should be produced even on nitrating benzene. The reduction in the amount of such fume, and the improvement of the yield of nitro-derivative effected by adding sulphuric acid, is doubtless attributable to the action already referred to of the acid in promoting the separation of the elements of water; sulphuric acid must be supposed, in fact, in such cases to act not merely as a dehydrating agent in maintaining the nitric acid concentrated, but to exert a specific influence on the course of change. Lastly, the resinous matters often formed in large amount on nitrating many phenols are, doubtless, products of the interaction of several molecules of the addition compounds, or of the keto-compounds formed from them in the first instance.

The non-production of resinous matters when sulphoacids are treated with nitric acid so as to form the corresponding nitro-compounds by displacement of the SO_3H group by NO_2 , a modification which often makes it possible to prepare nitro-compounds not obtainable by the direct action of nitric acid, is also elucidated by the author's theory; the addition compound formed in such a case would very readily break up into sulphuric acid and the nitro-derivative, thus—



DISCUSSION.

Mr. GROVES said that he had been much struck, when preparing dinitrobenzene from benzene which had been most carefully purified, on observing that a very appreciable quantity of trinitrophenol was produced; the theory of nitration put forward by the authors would fully account for this.

22. "A New Method of Preparing Nitro-Derivatives and the Use of Nitrogen Dioxide as a Nitrating Agent." By HENRY E. ARMSTRONG and E. C. ROSSITER.

Reference has been made in the foregoing note to the production from the compounds formed by the addition of the elements of nitric acid to the bromo-derivative of betanaphthol of nitro-derivatives of the naphthol on treatment with alkali, a bromine atom becoming displaced by NO_2 . As in this interaction a bromine atom is removed and an atom of hydrogen is added to the CO group, such a method of treatment obviously is scarcely that best calculated to effect the formation of the nitro-derivative, and, as a matter of fact, the nitro-derivative is not the only product. On treating the addition compound, however, with sulphurous acid, a practically theoretical yield of the nitro-naphthol is obtained; this method appears to be of general application.

The authors have been naturally led to study the action of nitrogen dioxide, NO_2 , on unsaturated compounds of various kinds, in the expectation of obtaining addition compounds which by loss of HNO_2 would pass over into nitro-derivatives of the substances treated. They find that such addition compounds are actually obtainable, and that, on treatment with alkali and reducing agents, they yield nitro-derivatives. Thus betanaphthol affords as much as 75 per cent of its weight of nitro-betanaphthol; alphanaphthol behaves similarly. In some cases, the addition compound is so unstable that it spontaneously decomposes; thus phenol at once yields a mixture of ortho- and para-nitrophenol. The authors propose to study the behaviour of unsaturated compounds generally towards nitric acid and nitrogen dioxide from the point of view indicated in this and the previous note.

23. "Nitrification. Part IV." By R. WARINGTON.

The first section of the paper describes early experiments, made in 1878—84, showing the existence of an agent producing only nitrites, and the means of separating it from soil. It was at first thought that the age of the culture was the factor which determined the loss of the power of producing nitrates, but this idea was negated by subsequent experiments. Successive cultivation in ammoniacal solutions, made permanently alkaline with disodium carbonate, was found to be a certain method of

obtaining a purely nitrous agent. Pasture soil yielded the nitrous agent more readily than arable soil.

The isolation and properties of the nitrous organism are next described. The gelatinous matter which appears under certain conditions at the bottom of old cultures was in 1883 examined microscopically, and found to consist of circular corpuscles imbedded in a zoogloea. In 1886 this jelly was spread on gelatin, but it yielded no nitrifying organism. In 1889 a systematic attempt at the isolation of the organism commenced. Successive cultivations were made in an ammonium carbonate solution, supplied with phosphates, &c., but containing no organic matter. A series of transparent cultures was obtained, containing only nitrites. These cultures were spread on gelatin and agar-agar, the composition of the jelly being made to correspond, as far as possible, with that of a nitrifiable solution. The later cultures yielded on gelatin one organism only, a short bacillus. This and all the other organisms obtained by cultivation on gelatin from nitrified solutions were seeded into both liquid and solid media susceptible of nitrification, but without result. Microscopical examination of the nitrified solutions showed that cocci were abundantly present, but these never appeared on the gelatin cultures.

The first attempts to separate the nitrous organism by the dilution method failed. By substituting an ammonium chloride solution with calcium carbonate for the ammonium carbonate, success was obtained in October, 1890, three nitrified cultures seeded with dilutions of $1/10,000$, $1/100,000$, and $1/1,000,000$, giving no growth on gelatin.

The nitrous organism thus obtained oxidises ammonia to nitrous acid, and has no effect on nitrites. It produces nitrous acid in solutions of asparagine, milk, urine, and urea. Grown in broth containing calcium nitrate, it does not reduce the nitrate to nitrite. It produces no turbidity or visible change when grown in broth or in any of the other solutions named.

The nitrous organism requires no organic matter for its nutrition; it is apparently capable of assimilating carbon from acid carbonates. The presence of either calcium or sodium acid carbonate distinctly favours nitrification; neutral sodium carbonate greatly hinders nitrification. The proof that carbon is assimilated from carbonates has been furnished by Winogradsky. The energy that is required for the decomposition of a carbonate is apparently furnished by the oxidation of ammonia on nitrogenous organic matter. Calcium acetate (0.25 grm. per litre) favours nitrification when only the nitrous organism is present.

The nitrous organism occurs as nearly circular corpuscles, varying from minute points up to nearly 1.0μ in diameter; these circular organisms stain deeply. It also occurs as oval cocci, the length frequently exceeding 1.0μ , the ends occasionally more or less truncated.

The remainder of the paper deals with the nitric organism. Results obtained in 1880-81 revealed the existence of an organism which energetically converted nitrites into nitrates, but was apparently unable to oxidise ammonia. In 1886 and 1890 attempts were made to separate the active organism from the 1881 cultures by growths on gelatin and potato; none of the organisms thus separated had any power of oxidising either ammonia or nitrites. Recent results show that the nitric organism develops freely in inorganic solutions containing potassium nitrite, phosphates, &c., especially if supercarbonates are present. Monosodium carbonate, 1-4 grms. per litre, exerted a very favourable influence, 6 grms. a retarding influence. Disodium carbonate greatly hinders its action.

The nitric organism produces neither nitrites nor nitrates in ammoniacal solutions, even when carbonic acid, or monosodium carbonate, or calcium acetate is supplied. In the absence of ammonia it energetically converts nitrites into nitrates; the presence of ammonia is apparently a great hindrance to its action.

An attempt to isolate the nitric organism by the dilution method failed, but apparently only one other organism (a stout bacillus growing on gelatin) was present in some of the cultures obtained. The stained preparations from these cultures contained an abundance of the minute circular organisms observed in pure cultures of the nitrous organism; the form of the two organisms is thus apparently similar.

The nitrification performed by soil thus appears to be the work of two organisms, one of which oxidises ammonia to nitrite, while the other oxidises nitrite to nitrate. The first organism is easily separated from the second by successive cultivations in solution of ammonium carbonate. The second is (probably) separated as easily from the first by successive cultivations in solution of potassium nitrite containing monosodium carbonate.

The paper was illustrated by micro-photographs, showing the nitrous organism as developed in ammoniacal solutions, milk, and broth; and the nitric organism grown in a solution of nitrite. The photographs were executed by A. Pringle, Esq., and Dr. Bousfield.

Discussion.

Prof. THOMSON, referring to the method of cultivation on gelatinised silica described by Mr. Warrington, said that the account given of the method reminded him of an observation made so far back as 1875; a solution of silica which he had prepared by dialysis had solidified, and he noticed, after a time, that a growth of what he thought was an ordinary mould had appeared on the surface; there could have been nothing present besides the silica, except traces of mineral salts.

Dr. MUNRO said that he was glad to see that his contention that organic matter was actually prejudicial to the growth of the nitrifying organism was now proved. Referring to the conclusion that two organisms were concerned, one of which converted the ammonia into nitrite, the other extending the oxidation to nitrate, he asked how those cases in which only nitrates were found were to be explained; it very rarely happened, for instance, that in well-waters the ammonia was converted into nitrate with intervention of nitrite. Perhaps two organisms were present, which did their work simultaneously.

Mr. WARRINGTON, in reply, said that the two organisms would have no difficulty in acting together in very weak solutions of ammonia.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxii., No. 22, June 1, 1891.

Calorimetric Researches on Humic Acid derived from Sugar.—MM. Berthelot and André.—The result of these researches is that humic acid is a polybasic acid capable of losing one part of its water of hydration by mere desiccation, and even in the midst of water at ordinary temperatures in virtue of true dissociation. In this state it combines with three equivalents of potassa, forming insoluble salts; the first is monobasic, very stable, formed with the liberation of +18 cal., *s.d.*, comparable to that of the solid alkaline salts formed by the most powerful mineral acids. The two equivalents of base which then unite to the first salt form a tribasic salt equally insoluble, but liberate much less heat. These humic matters, comparable to those of the soil, undergo thus, under the influence of a base, phenomena of hydration; then, by the inverse action of acids, effects of spontaneous hydration by dissociation—a series of effects in virtue of which

external energies should be continually introduced in the chemical reactions accomplished during the course of natural vegetation. Humic acid is formed from sugars with the liberation of heat, but this liberation expends only a portion of the thermic excess of these carbohydrates over carbon and water capable of being formed by total destruction. Hence it results that humic acid would be equally formed from carbon and water with absorption of heat, *i.e.*, that it contains an excess of energy capable of being expended in the course of the consecutive transformations which are effected either by purely chemical actions or with the concurrence of microbial agents.

Determination of the Molecular Weight at the Critical Point.—P. A. Guye.—A purely mathematical paper not susceptible of useful abridgment.

Detection and Separation of the Platinum Metals, and in Particular of Palladium and Rhodium, in Presence of the Common Metals.—A. Joly and E. Leidié.—(See p. 292).

On the Specific Heats of Some Solutions.—W. Timofeiew.—The author gives his results in the form of a table.

On the Oxidation-Products of Uric Acids.—C. Matignon.—A thermo-chemical study of allantoin, alloxane, and alloxanthine.

On the Use of Ammonium Selenite for the Diagnosis of the Alkaloids.—A. J. Ferreira da Silva.—(See p. 291).

MEETINGS FOR THE WEEK.

WEDNESDAY, 24th.—Geological, 8.

Society of Arts, 4. (Anniversary).

THURSDAY, 25th.—Chemical, 8. Extraordinary General Meeting.

Royal Society Club, 6.30. (Anniversary).

FRIDAY, 26th.—Royal Institution, 9. (Faraday Commemoration Lecture). Prof. Dewar, F.R.S.

Physical, 5. "The Construction of Non-Inductive Resistances," by Prof. W. E. Ayerton, F.R.S., and Mr. T. Mather. "The Influence of Surface-Loading on the Flexure of Beams," by Mr. C. A. Carus-Wilson. "On Pocket Electrometers," by Mr. C. V. Boys, F.R.S. "On Electrification due to the Contact of Gases with Liquids," by Mr. J. Enright, B.Sc.

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THE CHEMICAL NEWS.

VOL. LXIII., No. 1648.

ON A NEW DEPARTURE IN MATTE-SMELTING FOR COPPER AND SILVER IN REVERBERATORY FURNACES.

By W. BETTEL, Metallurgist and Chemist.

IN October last, owing to the smelting arrangements at the Willows Mine being unsatisfactory, I was asked by the managing director of the Company to take this department under my supervision, a handsome bonus being promised if I were successful. This, in the directors' opinion, I have now earned.

The absence of sulphur in our ores and fluxes (except in trifling amounts), and the presence of antimony exceeding the percentage of copper in the ores to be smelted, the copper existing as azurite and malachite—average 4 per cent copper wet, and 40 ozs. silver per ton (2240 lbs.)—the bulk of the ore being hydrated oxide of iron and antimonious compounds—made the problem of matte production one of difficulty at first sight.

Other difficulties I had to contend with. Bad coal, containing from 18 to 40 per cent ash, gave little heat in the furnace and much trouble (with the clinker) in the grate; huge accretions forming in that part of the grate level with the bridge. I found that it was the practice of the furnacemen, once every twelve hours, to pour water into the grate through holes in the roof, to cool the clinker, which was then removed by steel bars and sledge hammers; the furnace in this manner being cooled to such an extent that fully four hours were lost every day.

This led me to devise a method of burning this poor coal to advantage, at the same time preventing the formation of the huge masses of clinker which retarded operations. This accomplished, as will be seen from the context, there still remained one more difficulty.

When I took charge, although the furnace had been running five months, only about 4000 lbs. matte was obtained: opinion being divided as to whether the copper and silver went into the slags, or were, in some way, volatilised. My opinion, that the matte would be found in and beneath the furnace bottom, received no credence, and it was with the greatest difficulty that I persuaded the management to let me "flow out" the furnace and alter another one (not then started) in order to carry out my arrangements with forced draught, then to excavate the bottom, &c., from the cooled furnace (there being no vault), and rebuild on an improved plan.

It was then found that the matte had penetrated four feet six inches below the furnace bottom, into every conceivable crack and crevice, lumps of matte three or four inches in diameter, with cores of charcoal, being found here and there. For a time these appearances puzzled us, until in the soil, or "veldt," outside were found large roots, similar in shape to the lumps of matte. The roots had been carbonised and matte had flowed round the carbonised residue, assuming the shape of the original roots. Further, about four inches of each "bottom" was loose sand, proving that the temperature obtained in "smelting in" the bottoms and during the subsequent five months' smelting had been insufficient for ordinary operations.

About 60 tons of material, containing about 18 tons matte, was obtained in the excavation—every joint of the brickwork below the slag-line being a conduit for the conveyance of matte to the foundation. I had, therefore, to arrange a process for cooling the lower part of furnace

bottom, sides, and bridge by vaults and brick tubes, working under a forced draught with moist air. When the furnace was ready, I decided to melt the sand bottom in successive layers with a material that would cause its cohesion and impart a slight fusibility under intense heat to produce a bottom almost impervious to molten matte. Then, for the protection of the sides I found a substance to replace the "daagga"—a "mending" composed of mud and sand in some quartz, from abandoned workings, which I had crushed and mixed with yellow clay. This stood fairly well.

Drawing upon my experience in furnace-work at (1) Middlesborough-on-Tees, where I was in practice as a metallurgical chemist and public analyst for six years; at (2) The Sheffield Smelting Company's Establishment (Gold, Silver, Platinum Metals, Lead, and Copper Smelting, &c., Refining Works), and a similar establishment I had charge of in Birmingham, where, between the two, I had seven years' experience in silver, &c., smelting, and the advantage of an intimate acquaintance with the reduction of all classes of ores of gold, silver, copper, &c.; and (3) as smelting works manager at the New Morfa Copper and Silver Works, Swansea (Messrs. Williams, Foster, and Co., Ltd.), where I had charge of 30 smelting and refining furnaces, &c.,—I decided to adopt the following arrangements:—

1. To construct vaults as a foundation; over these a number of brick channels (suitably arranged along the whole width of the furnace), covered with bricks, rubbed joints and grouted, communicating to steam-blast arrangement at one corner (flue end) of furnace, to ashpit at outlets, and after cooling bridge, to "blowpipe jets" in bridge and roof.

2. To work the furnace under pressure with closed ashpit, using an injector arrangement similar to, but simpler than, the Körting's injector.

These gave me the following advantages:—(a) I could reduce the heat in the grate, making the ash loose and friable, and (b) transfer such heat as well as heat from furnace bottom abstracted by passage of air and steam through the brick tubes, in the form of hydrogen and carbonic oxide, to the laboratory—the hearth—of the furnace, where these gases are burnt with the hot blast from roof and bridge, producing an intense heat similar to that obtained in a Siemens regenerative gas furnace.

Having, by the brickwork tubes or channels, considerably reduced the usual depth between skimming plate and bottom, I smelted the bottom in three thin layers, the first two with sifted sand to which 1½ per cent lime was added and intimately mixed, and on these a seasoning charge of sharp slags smelted. The upper layer consisted of sifted river sand only, which, after smelting, was seasoned as before. During the smelting the heat had to be checked, as the bricks, although nearly as infusible as those of the Abernant (Dinas) Co., could not withstand the intense heat produced.

The next problem was to smelt refractory antimonial oxide and carbonate ores (70 per cent of which was delivered to furnaces in pieces from 2½–3 cubic inches), without sulphides, except in traces, and still produce clean slags, collecting 90 per cent at least copper and silver at one operation in the species of matte, or speiss, produced at a profit, coal being 50s. per 2000 lbs., stores generally about 500 per cent over English prices, and white labour £27 per month (furnacemen).

This I solved in the following manner. I selected as a type of slag, which would be as economical as any, Mr. Malvern W. Iles's type "C," containing about 27 per cent silica. This I produced by means of a flux. I found from one of our waste heaps out of the mine a silicious, ferrous, calcic, magnesian carbonate, containing 5 per cent and upwards of ar. hracitic carbon.

This, together with coal and "cobbing," and rich "sharp" slags composed the fluxing part of our charges. Owing to absence of suitable crushing appliances, the coarse ore we are compelled to put in the furnace takes a

considerable time to smelt, the heat of slag formation being proportionately high; otherwise, judging from the fluid slag produced and its comparatively low melting-point, were we able to more thoroughly mix our charges the capacity of our furnaces would be doubled. However, three charges are smelted in 24 hours in each furnace, *clean slags are produced*, the copper and silver are converted into a "matte"—*antimony being the collecting agent in place of sulphur*—and 90 per cent of copper and silver is recovered.

My explanation of the changes involved is as follows:—Oxide of antimony fluxed with lime and magnesia will dissolve in a bath of basic ferrous silicate, and be reduced by carbon conjointly and simultaneously with copper and silver, forming a fusible and brittle antimonide of copper and silver, with a formula of Sb_2Cu_3 —provided that the slag does not contain more than 5 per cent magnetic oxide of iron; otherwise the slag is rich, copper and antimony are lost, and some silver volatilised. Excess of carbon is avoided as tending to throw down metallic iron, making the matte coarse and difficult to break.

After satisfying myself that the bottom of No. 1 furnace was in working order I commenced to smelt, and found after three charges that I had saturated the bottom of a 3-ton furnace with 500 lbs. of matte, instead of 36,000 lbs. which was lost in the old furnace. The bottom, at the time of writing, is an excellent order, and the furnace is delivering over 90 per cent copper and silver in form of "matte."

We concentrate for 35 ozs. ores 16½ tons of ore, or 27½ tons of charge, into 1 ton matte = 91.3 per cent of silver recovered; about 7.5 to 8 per cent going into slags, and the remainder volatilised. We should consider on 35 ozs. ore 80 per cent recovery fairly good, and this was the percentage of extraction I had agreed to accomplish. The average composition of slags and "matte" is seen from the following analyses I have made from No. 1 furnace:—

Slag.	
Silica	= 27.05 per cent.
Ferrous oxide	= 53.30 "
Ferric oxide	= 2.55 "
Alumina	= 4.50 "
Manganous oxide	= 3.00 "
Phosphoric acid	= 0.21 "
Arsenious acid	= 0.055 "
Antimonious acid	= 0.130 "
Cuprous oxide	= 0.45 "
Silver	= 0.005 "
Sulphur	= 0.05 "
Bismuth oxide	= 0.10 "
Lead oxide	= 0.45 "
Lime	= 5.32 "
Magnesia	= 2.80 "

Total .. = 99.97 "

"Matte."	
Copper	= 52.50 per cent.
Antimony	= 38.00 "
Arsenic	= 2.00 "
Sulphur	= 2.06 "
Iron	= 3.60 "
Lead	= 0.25 "
*Silver	= 1.59 "

Total .. = 100.00 "

* = 530 ozs. silver per ton of 2240 lbs.

The silicious iron magnesian limestone is fairly represented by the following analysis, although the material is far from uniform in composition:—

Insoluble matter—	
principally silica }	 = 37.40 per cent.
Alumina, with trace of }	 = 2.94 "
manganese oxide }	 = 9.57 "
Ferrous carbonate	= 30.40 "
Calcic carbonate	= 8.92 "
Magnesian carbonate	= 5.77 "
Water and volatile matter..	= 5.00 "
Carbon (anthracitic)	= 5.00 "

Total .. = 100.00 "

The antimonial copper matte we produce, by an oxidising treatment in a special form of hot blast reverberatory furnace, yielded a crude copper (in shot) for silver extraction, assaying:—

Copper from "Matte."	
Copper	= 93.55 per cent.
Antimony	= 1.31 "
Arsenic	= 0.60 "
†Silver	= 3.26 "
Oxygen and other sub-	
stances not estimated }	= 1.28 "

Total .. = 100.00 "

† = 1064.9 ozs. per ton of 2240 lbs.

—containing practically all the silver—the slag containing about 15 ozs. per ton silver, and also 12 per cent of the copper and 10 per cent antimony in original matte. The remainder of antimony volatilised.

Although at the Willows Copper (Arg.) Syndicate's Works it was inconvenient to interfere with the arrangement of flues, still the steam for steam blast may be raised by means of heat from waste furnace gases (as is done in iron and steel works). Here we use an 8 horsepower locomotive boiler to supply steam-blast to two furnaces. This boiler consumes 800 lbs. coal for twenty-four hours, delivering steam at 20 lbs. pressure through four jets ½ inch (bare) diameter—two to each furnace. The influence of steam in preventing the formation of all except "rotten" clinker is most marked, and with my arrangement the commonest coal can be made to yield good results, whilst with good coal the increased duty obtained (especially with the arrangement for heating the moist air) is very striking. Another peculiarity is, that the coal is burnt to a clean ash, and the only coal or coke which falls through the bars is during grating, and that is small in amount.

By adapting this furnace to copper-smelting, any grade of matte within reasonable limits may be obtained according to the character of flame produced, which may be altered at will from reducing to oxidising or neutral by suitable valves in the air passages, while for metal or regulus-roasting and copper-refining it could not be surpassed for ease (and cheapness) in working.

There is a modification of this hot-blast reverberatory furnace—for civilised places where decent iron castings and wrought iron fittings are procurable at reasonable rates—which I propose to work elsewhere if opportunity occurs. This plan embraces water-jacketing portions of the furnace most exposed to wear, and does not need more than a few inches of foundation (concrete)—no vault needed. From results already obtained I expect this furnace to be more economical than a gas furnace with regenerator, and, with certain modifications, would be found applicable to any operation requiring an intense, heat, which may be made oxidising, neutral, or reducing at will.

The Willows Copper (Arg.) Mine,
near Pretoria, Transvaal, South Africa,
March 27, 1891.

The Metallurgy of Steel.—The Société d'Encouragement pour l'Industrie Nationale, of Paris, France, has awarded a prize of 2500 francs to H. M. Howe for his work on "The Metallurgy of Steel," lately reviewed in these columns.

NOTE ON A VOLATILE COMPOUND OF
IRON AND CARBONIC OXIDE.*

By LUDWIG MOND, F.R.S., and FRIEDR. QUINCKE, Ph.D.

IN a paper on the action of carbonic oxide on nickel, communicated to the Chemical Society (*Journal*, lvii., 749, 1890) by us in conjunction with Dr. Carl Langer, and which dealt with the preparation and properties of nickel-carbon oxide, it was stated (p. 752) that all experiments to obtain a similar compound with other metals had been unsuccessful. Considering it very improbable that nickel should be the only metal forming such a compound, we have continued these experiments, more particularly with iron, under very varied conditions, and have at last succeeded in volatilising notable, although very small, quantities of iron in a current of carbonic oxide.

If very finely divided iron, obtained by reducing iron oxalate in a current of hydrogen at the lowest possible temperature, exceeding but little 400° C., is allowed to cool in hydrogen gas to 80° C., and then treated with carbonic oxide, the issuing gas imparts a yellow colour to the flame of a Bunsen burner into which it is introduced, which continues, even at ordinary temperature, for several hours; and by passing it through a heated glass tube a metallic mirror is formed at between 200° C. and 350° C., while at higher temperatures black flakes are formed.

On dissolving these mirrors the solutions gave all the known reactions of iron in remarkably brilliant colours. The oxide obtained by dissolving the mirror in nitric acid, precipitating with ammonia, and heating to constant weight, was reduced by hydrogen. We obtained from 0.4342 gr. of oxide 0.3037 Fe = 69.93 per cent. Fe = 56, O = 16 require 70.00 per cent. There can thus be no doubt of these mirrors consisting of iron. The black flakes obtained at higher temperature consist of iron and carbon. By the combustion of the substance and absorption of the carbonic acid formed in caustic potash, we found 79.30 per cent of carbon.

However, even under the most favourable circumstances, the quantity of iron obtained in this way has been very small. Treating 12 grms. of finely divided iron with carbonic oxide during six weeks, we volatilised only about 2 grms. of iron. As the action of the carbonic oxide became less energetic, after a time we had to interrupt the operation and heat the iron to 400° C. in a current of hydrogen for about twenty minutes every five or six hours. By passing 2½ litres of carbonic oxide per hour over the iron, the issuing gas contained at its best not more than 0.01 gr. of iron, which corresponds (if we assume the volatile iron compound to have the same composition as nickel-carbon oxide) to less than 2 c.c. of the compound in a litre of gas.

This great dilution makes the study of the properties and composition of the compound very difficult.

In passing the gases containing it through sulphuric acid the compound is completely absorbed, but the solution decomposes very rapidly.

In passing the gases through benzol or heavy mineral or tar oils the compound is partially absorbed, but all the substances we have tried only take up a small quantity

of it. The solutions obtained are of a tawny colour, and decompose on exposure to the air, with separation of iron hydroxide.

The solutions in mineral oils boiling between 250° C. and 300° C. seemed to us the most suitable for studying the composition of the compound; but we found it impossible to exhaust it from these solutions by means of the vacuum pump.

On raising the temperature of the solution to 100° C., the solution remained clear, and under a vacuum of 500 m.m. mercury we obtained only a small quantity of a mixture of air and carbonic oxide (from 30 c.c. of oil about 5 c.c. of gas).

On raising the temperature to 180° C. the solution turned black from separated metallic iron, which was found free from carbon, and carbonic oxide was slowly evolved, which sometimes contained a very small quantity of carbonic acid, but was always quite free from hydrogen.

We have determined the quantity of iron and carbonic oxide obtained by heating about 30 c.c. of heavy mineral oil, through which the gas containing our compound had been passed from 8—16 hours in a glass vessel very nearly filled with the oil and connected by a capillary tube to a Hempel burette filled with mercury.

The tube was heated to 100° C. under a vacuum of 500 m.m. mercury, until the volume in the burette remained constant. The tube was cooled down to measure the exact volume of this gas, and was then heated up to 180° C. until no more gas was evolved, which took from 1—2½ hours. The increase in the volume of the gas by the latter operation gave us the carbonic oxide in the compound.

The iron contained in the oil was, if necessary after dilution with ether, collected on a filter and converted into oxide. The filtrate was distilled off, and the small residuum treated with hydrochloric acid and precipitated with ammonia, and the resulting small quantity of oxide of iron added to the first. In this way we obtained the following results:—

These figures, although only approximate on account of the very small quantities of substance and the imperfect method we had to use for their determination, make it very probable that the volatile iron compound is iron tetracarbonyl [Fe(CO)₄], analogous to nickel tetracarbonyl [Ni(CO)₄].

METHOD OF DETERMINING INDIGOTINE
FOR COMMERCIAL PURPOSES.

By F. A. OWEN.

UNDER the above heading the author published a paper in the *Journ. Amer. Chem. Soc.*, in November, 1888. The process as there described has been materially modified, and as now practised in the mills of the Burlington Woollen Company, at Winooki, Victoria, is as follows:—

From the sample shave off and coarsely powder 2 or 3 grms., from which weigh with exactness two portions of 1 grm. each. In the first determine the moisture by drying in a watch-glass at 100° C., and afterwards ignite this portion and determine the ash. The second portion

No.	Solvent.	Found.		Corresponding to.		1 atom Fe to 4 atoms CO.	Calculated.	
		Increase of volume.	Fe ₃ O ₄ .	CO.	Fe.		Proportion of atoms CO to 1 Fe.	Quantity absorbed of Fe(CO) ₄ = ½ CO.
		C.c./760 m.m.	Grm.	Grm.	Grm.	Grm.		
1.	Paraffin oil.	31.32	0.0270	0.03917	0.01890	0.01958	4.144	7.83
2.	Petroleum oil.	34.29	0.0304	0.04288	0.02128	0.02144	4.030	3.57
3.	"	20.2	0.0174	0.02527	0.01218	0.01263	4.150	5.05
4.	Kerosine.	38.18	0.0320	0.04775	0.02240	0.02387	4.264	9.54
5.	"	50.45	0.0446	0.06310	0.03122	0.03155	4.042	12.61

* A Paper read before the Chemical Society, June 15, 1891.

is brushed from the scale-pan directly into a glass mortar, ground for a time dry, then water is added and the grinding is continued for some time; the pestle is rinsed into mortar, and the whole allowed to settle for a minute or so, and all that will freely pour off is decanted into a glass-stoppered 200 c.c. flask. The sediment is re-ground with water, and decanted as before until the whole has been transferred. Three grms. of zinc dust and 60 c.c. of commercial strong ammonia are now added; then the flask is filled to $\frac{1}{4}$ c.c. above the mark and shaken. Reduction takes place in from half an hour to two hours, during which time it should be shaken occasionally. When the reduction is complete the froth will subside and the solution become pale yellow, or, with some samples which contain chlorophyll or some non-reducible green colouring matter, greenish yellow. Then remove with a pipette 50 c.c. to a beaker or porcelain dish, add 5 or 6 drops of ether, and agitate by blowing air through with the pipette until most of the indigotine is precipitated. Acidify in moderate excess with HCl, heat to boiling, and pass through a tared filter; dry at 100° C., and weigh. It is not necessary to take any special care to prevent absorption of moisture while weighing, only the filter paper must be, as nearly as possible, in the same condition as when tared. The results are accurate. The lots when bought and re-tested should show no variation from the sample except in the percentage of moisture, which will be higher than in the sample. Indigo often loses 20 per cent in drying, and not unfrequently yields 80 per cent of indigotine, after drying. — *Four. Amer. Chem. Soc.*, Jan., 1891.

SOME CHEMICAL PRODUCTS OF BACTERIAL GROWTH, AND THEIR PHYSIOLOGICAL EFFECT.

By E. A. VON SCHWEINITZ,
Chemical Laboratory, Bureau of Animal Industry, Washington, D.C.

For a short time I have been engaged in studying the chemical products formed by the hog cholera and swine plague germs by their growth in artificial culture media, and have succeeded in isolating an albumose and ptomaine from each.

To distinguish the products the names *sueholotoxin* and *suehocolalbumin* have been given to the substances from the hog cholera cultures, and *suplagatoxin* and *suplagoalbumin*, respectively, from the swine plague cultures.

The albumoses are white, pulverulent substances, soluble with difficulty in water, and precipitated from this solution by absolute alcohol. They can be obtained in crystalline plates by drying over sulphuric acid, *in vacuo*.

The ptomaines are best obtained in the form of the double platinum salts, as the hydrochlorides are difficultly crystallisable. These double salts are very light yellow in colour, readily soluble in water, difficultly so in alcohol, and appear under the microscope as needle-like crystals. (Specimens of the albumoses and platinum salts were exhibited).

A subcutaneous injection of a small quantity of these substances is sufficient to produce death in guinea pigs in from 24—48 hours.

If, however, a much smaller quantity is injected, and the injection repeated a number of times, the animals are protected from the corresponding disease when communicated by direct inoculation with the germ. In quite a long series of experiments the check animals invariably died, while the treated ones recovered after inoculation with the germ.

More recently, Dr. W. H. Gray, of Washington, and myself have conducted some experiments upon guinea-pigs, and succeeded in producing great resistance, and subsequently immunity from diphtheria, by first treating

the animals with the chemical products obtained from cultures of the germ.

There is every reason to hope that these results can be turned to practical application in the diseases of both animals and men. — *Four. Amer. Chem. Soc.*, Jan., 1891.

NOTES ON THE ESTIMATION OF NITROGEN IN NITRATES BY KJELDAHL'S METHOD.

By LYMAN F. KEBLER.

In the history of analytical chemistry no method has been so universally adopted, in so short a time, as the "Kjeldahl Method" for the estimation of nitrogen. The fundamental reactions in the method, according to Dafert (*Ztschr. Anal. Chem.*, 1888, 27, 222), are as follows:—First, the sulphuric acid abstracts from the nitrogenous organic material the elements of water and ammonia gas, forming ammonium hydrate, and subsequently ammonium sulphate; second, the sulphurous anhydride which is evolved reduces the nitrogenous compounds, but this is insignificant as compared with the first reaction.

The original method is not applicable for the estimation of nitrogen in all inorganic and organic combinations; but the method has been modified to such an extent that the nitrogen in almost all inorganic and organic combinations can be estimated by it.

The method, as followed by the writer, is given in detail in Bulletins Nos. 19 and 24 of the U.S. Agricultural Department.

The instructions which were followed did not indicate how the distillate should be received in the receptacle.

After making a series of experiments, the writer found it necessary to connect the end of the condenser with the receptacle by a glass tube dipping below the liquid contained in the receiving flask.

While working with this method, the writer observed that whenever the sulphuric acid was added to some material containing nitrates, nitric acid was evolved, and could be detected by its odour at the mouth of the flask. It was plainly evident that this must be overcome in some way. It was observed that when the sulphuric acid was added quickly and the flask shaken moderately, none, or very little, of the nitric acid escaped from the sulphuric acid; none escaped from the flask.

After this observation, a series of experiments were made, with the following results:—

1st. The sulphuric acid was added slowly in *sight** different experiments, when the maximum amount of nitrogen obtained was 16.03 per cent; minimum, 15.91 per cent; average, 15.97 per cent.

2nd. The sulphuric acid was added quickly in *twenty-six* different experiments, when the maximum amount of nitrogen obtained was 16.33 per cent; minimum, 16.03 per cent; average, 16.18 per cent.

The smaller the quantity of material employed, the greater the percentage obtained. In the above experiments as uniform a quantity of material as possible was employed.

If the sulphuric acid converts the nitrogen into ammonia, why add the potassium permanganate? From a large series of experiments, the writer concludes with Lenz (*Ztschr. Anal. Chem.*, 1887, 26, 590), that the potassium permanganate when added to a hot mixture destroys the organic compounds still remaining, and if the digestion is carried far enough all of the nitrogen is then converted into ammonia.

Of what value is the addition of metallic oxides or metals? The time consumed for complete oxidation when a metal or metallic oxide was added varied from *two to four hours*, while without the addition of these

* The work was all done on sodium nitrate

from ten to thirty hours were required for complete oxidation. In order that a method be practicable, its execution must require as little time as possible.

During the first part of the work, to prevent bumping, metallic zinc was used, but was soon found to be entirely unnecessary, especially when a Fletcher's circular burner was employed.

The results obtained by Kjeldahl's method were found by the writer to be a trifle lower than those obtained by the absolute method, agreeing very closely with those of Ruffie's method. The absolute method yielded, from twelve combustions, an average of 16.28 per cent, while the Ruffie's method yielded, from ten combustions, an average of 16.16 per cent. By comparing the above results, it was concluded:—

1. The Kjeldahl method is not as accurate as the absolute method for estimating nitrogen in nitrates, but is executed in much less time, since many estimations can be made at the same time, and is applicable for all practical purposes.
2. It is necessary to add the sulphuric acid quickly, that there may be no loss of nitric acid.
3. The end of the condenser must dip into the liquid contained in the receiver.
4. In order to economise time, a metal or metallic oxide must be added.
5. The potassium permanganate must be added to complete oxidation.
6. It is entirely unnecessary to add metallic zinc to the contents of the distillation flasks, to prevent bumping, especially when a Fletcher's circular burner is at hand.—*Journal of Analytical and Applied Chemistry*, Vol. v., No. 5.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1891.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, *Metropolis Water Act*, 1871.

London, June 10th, 1891.

SIR,—We submit herewith the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined, the whole were found to be clear, bright, and well filtered.

The condition of the water supply to the Metropolis during the month of May was throughout entirely satisfactory, and was characterised more especially by the marked degree of freedom from brownish tint of the water, and by the great uniformity of composition and character among the different samples examined. Thus the mean amount of organic carbon present in the

Thames-derived supply being 0.136 part, the maximum amount in any single sample examined was found to be only 0.150 part in 100,000 parts of the water.

The following Table shows the comparable results furnished by the examinations of the Thames-derived water made during the past three months respectively:—

Thames-derived Supplies.

	Ratio of brown to blue tint.	Oxygen required for oxidation.	Organic carbon per 100,000.	Organic carbon per 100,000.
	Means.	Means.	Means.	Maxima.
March..	14.1 : 20	0.049	0.146	0.209
April ..	13.9 : 20	0.055	0.155	0.190
May ..	9.6 : 20	0.042	0.136	0.150

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 294).

Apparatus.

ANY microscope, the magnifying power of which can be modified from 50 to 200 diameters, is suitable for micro-chemical work. Nicol prisms are a desirable appendage, as also a microgoniometer. On the contrary, the chemist can easily dispense with lenses which serve for observations in convergent polarised light. Complicated appliances for illumination are as useless in the applications of the microscope to chemical research as are slides and fine screws on the work-table.

A microspectroscope may do good service, but can be but rarely used, as its arrangement takes much time. More useful is a microscope lamp for illuminating objects from above, which is otherwise difficult and imperfect. An essential condition is the largest possible distance of the objects. This makes work easy, and contributes to preserve the instrument from injury. I work generally at a distance of 3 c.m. when the magnifying power, according to the eye-piece, varies from 35 to 50 diameters, and when objects of 3 c.m. in length and breadth can still be seen at once. With so great a distance of the object a protection for the lowest object-glass is required only in particular cases. Frequently rinsing and cautiously wiping the lens with filter-paper free from dust or pure soft linen is sufficient to keep it in good condition for years. Certainly I wish hydrogen sulphide to be entirely banished from the room in which micro-chemical work is performed, and ammonium sulphide to be used there only exceptionally and immediately removed again. Hydrochloric and nitric acids at the degree of dilution and the small quantity in which they are used require special precautions only when working with high magnifying powers. Hydrofluoric acid and ammonium fluoride in acid solutions require precautions even at great distances. To cover the trial-drops with flat watch-glasses or microscopic covering-glasses is tedious and sometimes inadmissible. The lowest objective glass may be easily covered under all circumstances. A drop of water or glycerin is first placed on the lens, and then a round covering-glass of the smallest sort, or instead a round disc of mica which has been cut with a sharp cork-borer out of a thin, perfectly transparent leaf. Fragments of covering-glasses may also be used, though they are liable to be displaced or pushed off. As a matter of course, object-glasses which have been covered in this manner

* *Zeit. Anal. Chemie.*

must be washed and wiped before the instrument is put away. Powers which exceed 300 diameters involve so much inconvenience, and for inexperienced operators so much uncertainty, that I should like to see them as far as possible dispensed with in micro-chemical work.

As a test-object for the lowest object-glass there may be used a precipitate of potassium or ammonium chloroplatinate (dilution of the platinum solution 1:100); for the highest objective, a precipitate of ammonium magnesium phosphate (from solution containing 0.05 per cent of magnesium), or a crystallisation of silver chloride from an ammoniacal solution containing 0.05 per cent silver.

Along with the microscope we must mention the slides, which serve, not merely as a support in microscopic examination, but have to serve also as a test-tube or an evaporating capsule in preparing the object. The stages which the author has obtained are thin enough and well annealed. If carefully handled they may be heated up to 300° over a naked flame. Now and then one will fly, whence it is prudent to have a small stock in reserve, and to work over a porcelain tray or plate to prevent loss. Besides the glasses of the customary form (76 by 26 m.m.) shorter ones are needed, which are obtained by cutting the full size in half. They serve for covering preparations, and are useful in sublimations. For both purposes the corners are rounded off in the blast flame, and pressed so that they are turned down for about 1 m.m. A small stock of microscopic covering-glasses is also needful. They serve chiefly for heating and concentrating very small quantities of liquid in cases where a strong heat is desirable without complete desiccation. Square glasses of 18 m.m. length in each side are suitable.

For reactions with hydrofluoric acid, hydrofluosilic acid, and soluble fluorides, the stage-glass must be covered with a thin film of hard Canada balsam. The simplest and most expeditious method is to evaporate down the Canada balsam upon the glasses themselves. But in this manner it is not easy to obtain an even surface without wrinkles and scars. A faultless film is obtained if the balsam is heated until it becomes thinly fluid, and after it has been spread out evenly it is left to evaporate at the ordinary temperature of a dwelling-room. Several weeks are required for complete hardening. The end is reached more quickly with a solution of balsam in ether or carbon disulphide. For this purpose Canada balsam is evaporated in a flat capsule at about 120° until it scarcely froths, and a portion when allowed to cool scarcely takes an impression from the finger-nail. The mass after being coarsely powdered is dissolved to the consistence of olive oil. The glasses are then gently heated, covered with the liquid, which is quickly drained and shaken, and are then allowed to harden at the temperature of the room. Etheral solutions readily become stratified and grow dull by including watery vapour. In moist air this may also happen with carbon disulphide. Subsequent heating on the water-bath does not always remove the evil. The layer is sufficiently hardened in ten minutes, so as to bear washing and gentle wiping. It resists dilute acids for a considerable time, but it is quickly softened and rendered dull by dilute potassa-lye, and even by ammonia.

(To be continued).

The Telethermometer.—Prof. Puluj (*Chem. Zeitung*).—By means of this instrument it is said to be possible to measure the temperature of distant or inaccessible objects.

A Physician on Educational Cram.—Says Dr. B. W. Richardson, in the *Asclepiad*, "In our money-grubbing, fee-gulping, pedantic days, with their hide-bound educational formulae, John Hunter would have been nowhere. The very college where he is worshipped would have plucked him. Happy for him and for us that working in freedom from the tyranny of cramming his mind was permitted to run without impediment its immortal course."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

June 4th, 1891.

WILLIAM CROOKES, F.R.S., Vice-President, in the Chair.

MESSRS. F. Stanley Kipping and Mr. Ernest F. Hooper were formally admitted Members of the Society.

Certificates were read for the first time in favour of Messrs. William A. S. Calver, 45, Barrington Road, Brixton, S.W.; John William Heap, 33, Upper Gloucester Place; Robert Lennox, 3, Inverness Terrace, Putney, S.W.; Rudolf Laurentz Leffler, 21, Havelock Street, Sheffield; Charles K. Scott, 26, Pigott Street, Limehouse, E.; Thomas Stephenson, Bellasis Road, Byculla, Bombay; Henry White, 8, Brown Street, Masboro', Rotherham.

The following papers were read:—

24. "*The Molecular Refraction and Dispersion of Various Substances in Solution.*" By Dr. J. H. GLADSTONE, F.R.S.

The paper is a continuation of that laid before the Society in March last, and deals entirely with solid and gaseous substances that have been dissolved in water or other liquids for examination.

The results are given in several tables. It cannot be expected that there should be anything like the same accordance between the experimental and calculated numbers as is usually found in the case of pure liquids, as in weak solutions the experimental error is greatly multiplied. Nevertheless, in the case of organic compounds, the agreement is frequently very close. Terpene hydrate and terpine dihydrochloride appear as saturated compounds, and so do camphor and its derivatives; but benzyl camphor, $C_{17}H_{22}O$, and benzal camphor, $C_{17}H_{20}O$, substances recently prepared by M. Haller, give results, especially in dispersion, which are far in excess of what might have been anticipated. The sugar group presents some peculiarities. Cane sugar seems to show a refraction, and especially a dispersion, rather smaller than theory. Milk sugar, dextrose, and glucose are fairly accordant with theory; while mannitol, on the other hand, seems a little high in refraction.

Hydrogen chloride, bromide, and iodide give figures for the molecular refraction and dispersion much higher than the sum of the hydrogen and the halogen as determined from the paraffin compounds, and the values rise as the dilution becomes greater. Peculiarities analogous to this had previously been discovered by Perkin in regard to their magnetic rotation. Selenious and selenic acids, like the analogous sulphur compounds, afford optical values vastly less than what would be expected from the known values of their constituents. Metaphosphoric acid does the same.

The data relating to solutions of salts and alkalis, including compounds of aluminium, ammonium, barium, calcium, cerium, chromium, didymium, iron, iridium, lead, lithium, lanthanum, magnesium, potassium, silver, sodium, and tin. It will afford material for a revision of the refraction equivalents of the different metals, and of the electro-negative elements with which they are combined. They will also furnish additional means for determining the dispersion equivalents. Among the points noted are the following:—Ammonia, in strong contrast with the hydrides of chlorine, bromine, and iodine, appears to be uniform in its optical properties, whatever the strength of the solution; it agrees with what would be expected from theory. The refraction equivalents of cerium, didymium, and lanthanum are deduced from their salts at about 12.4, 16.4, and 15.5 respectively. The chlorates, bromates, and iodates are sufficiently represented to give an idea of their optical characters. At first sight it would appear that the

addition of 30 to the haloid salts causes an inadequate increase of the molecular refraction, and a slight actual decrease in the molecular dispersion. But this probably arises from the fact that the haloid salts themselves, when dissolved in water, give a somewhat excessive value. The molecular refraction for ClO_3 in its salts dissolved in water comes out at about 18.3, that for BrO_3 at 24.9, and for IO_3 at 33.8.

DISCUSSION.

Dr. PERKIN remarked that there was a close agreement between Dr. Gladstone's conclusions and those which he had arrived at from the study of magnetic rotatory power. The very high values afforded by the elements sulphur and phosphorus, in comparison with the values deduced for these elements from sulphuric and phosphoric acids, were very striking. The magnetic rotatory power of caustic soda was also very high.

Dr. GLADSTONE, in the course of remarks on Dr. Perkin's comments, said that it was particularly noteworthy that sulphur retained its high value in carbon bisulphide.

25. "The Nature of Solutions as Elucidated by a Study of the Densities, Heat of Dissolution, and Freezing-points of Solutions of Calcium Chloride." By S. U. PICKERING.

The curves representing these properties were examined in the same way as those representing various properties of sulphuric acid, and similar conclusions are drawn in the two cases, namely, that definite changes of curvature occurs at certain points which are the same, whatever property is examined, and which coincide, in all cases where such a coincidence can be ascertained with certainty, with simple molecular proportions of the salt and water; and consequently, that these changes represent the existence of hydrates in solution. The simplest hydrates indicated in the present case consist of CaCl_2 with 6, 7, and $8\text{H}_2\text{O}$; more complex hydrates exist also, as in the case of sulphuric acid.

26. "Notes on a Recent Criticism by Mr. Sydney Lupton of the Conclusions Drawn from a Study of Various Properties of Sulphuric Acid Solutions." By S. U. PICKERING.

Mr. Lupton (*Phil. Mag.*, xxxi., 418) applies a single parabolic equation to a portion of one of the author's sulphuric acid density curves, where a change of curvature was supposed to exist, and shows that it represents the results accurately if the experimental error is of a certain magnitude. This magnitude, however, is between 1000 and 10,000 per cent greater than the ascertained magnitude, and the equation, moreover, represents all the errors of like signs as being grouped together. Such a representation cannot disprove the existence of the particular change of curvature under investigation, still less that of the 101 others shown in the various curves examined by the author. The hydrate on which Mr. Lupton considers that his investigation throws "very grave suspicion" happens to be the one which the author has isolated in the crystalline condition.

DISCUSSION.

Professor RAMSAY doubted the validity of Mr. Pickering's methods of differentiating his curves. His own experience was that it was impossible to obtain results nearer than 2 or 3 per cent to the truth, with a curve drawn as carefully as possible, and a straight steel-edge laid along it to obtain tangents. Mr. Pickering, on the other hand, pursued a much more crude method, viz., he directly connected his experimental points by straight lines, and took the slopes of such lines as the tangents to his curves. This obviously did not eliminate any experimental error, but rendered it more marked.

Dr. ARMSTRONG said that he had no desire to intervene in the discussion which had arisen as to the validity of Mr. Pickering's method. It appeared to him, however, that Mr. Pickering's conclusions were in many respects open to question from a chemist's point of view; he thought, in fact, that Mr. Pickering both proved too much

and was illogical. Prepared as the speaker was to believe in the existence of hydrates in solution, he could not imagine that so large a number as was suggested would arise, or that the 102 breaks in the sulphuric acid curves, for example, could possibly be interpreted as evidence of as many distinct hydrates. There was no independent evidence to support such a conclusion.

Then he thought Mr. Pickering was illogical, because he interpreted all the breaks as indicative of hydrates, notwithstanding that he asserted—doubtless with justice—that both water and sulphuric acid in the pure state consisted of complex molecules: surely in this case, as change would set in at either end of the curve, it must be impossible to say which of the breaks are to be regarded as indicative of change in the composition of the complex molecules of acid and water respectively, which are due to the formation of hydrates consisting of simple water and acid molecules, and which are due to the formation of hydrates, say, of simple water and complex acid molecules.

With regard to Mr. Pickering's contention that Mr. Lupton must be wrong, because the latter had dealt with the part of the curve which included that hydrate which of all others was the best characterised hydrate of sulphuric acid,—a hydrate that he had prepared before them in the room,—Dr. Armstrong said that, from experiments which were being carried on in his laboratory, he was inclined to believe that the said hydrate probably did not begin to form in solution until the temperature sank to within a few degrees of its point of fusion: it might well be, therefore, that it was not present in the solution to which Mr. Lupton's conclusions related.

The more the speaker studied these questions experimentally, the more inclined he became to think that changes of composition, whenever they occurred, were indicated on curves drawn directly to represent the experimental results.

Dr. MORLEY said that it appeared to him that, even if Mr. Pickering was correct as to the number and position of breaks in the curves, it by no means followed that he had proved the existence of the particular hydrates suggested. A break in the curve should indicate that some new hydrate had just begun to form, but need not show what that hydrate was. Thus it was probable the hydrate $\text{CaCl}_2 \cdot 8\text{H}_2\text{O}$ would begin to form before the entire liquid contained a percentage of calcium chloride corresponding to that formula; and when the liquid had attained that composition, it might be expected to contain, besides the hydrate $\text{CaCl}_2 \cdot 8\text{H}_2\text{O}$, also higher and lower hydrates, such as $\text{CaCl}_2 \cdot 9\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 7\text{H}_2\text{O}$.

Professor RÜCKER, while fully admitting that the concordance of the numbers obtained by Mr. Pickering from observations on different physical properties of the solutions might fairly be urged in his favour, thought it important that the agreement between results all of which depended on the application of the same method should not be regarded as conclusive evidence in its favour if it were otherwise open to grave doubt.

In reality, Mr. Pickering's results were obtained, not by calculation, but by a method of observation and experiment applied to curves, which themselves represented the results of other experiments. The instrument used was a flexible ruler. It was admitted that the curves had to be specially drawn and the scale of the co-ordinates carefully chosen, if the results were to be satisfactory, and it was difficult to believe that the conclusions arrived at did not in large measure depend on the details of this preliminary adjustment.

At all events, as in the case of all other experimental methods, the final test of validity is whether concordant results are obtained by different observers, and it was therefore important that those who had personally tested it should give the results of their experience.

The speaker had himself gone over Mr. Pickering's work in the case of one of the sets of observations on the densities of dilute sulphuric acid of different strengths,

and he could bear witness to the care with which the curves were drawn. Nevertheless, the conclusion he arrived at was precisely similar to that which Professor Armstrong had expressed,

In the case of the more striking changes in direction and curvature which were clearly visible in the original curve, the various differential curves did not add much to the information it supplied. On the other hand, he thought that the evidence afforded by these secondary curves of changes of curvature, which could not otherwise be detected, was of the most untrustworthy character.

The assumption seemed often to be made that, because the results of experiments were more closely represented by two curves than by one, there must be a discontinuity, which was evidence of some physical change. That this conclusion might be fallacious is evident from the fact that, if a sufficient number of discontinuities were admitted, the results of experiment might be represented graphically with absolute fidelity.

His experience of the method would lead him to doubt any conclusions based upon it alone and not supported by independent evidence. It became untrustworthy just when it professed to become useful, by supplying information which could not otherwise be attained.

Mr. PICKERING said that Mr. Lupton's equation represented the rate of change of the densities as a straight line, while the figure which the actually observed rate of change formed was as different from a straight line as could well be imagined (*C. S. Trans.*, 1890, 80). The straight line might be regarded as fitting a greater or smaller portion of this experimental figure, according to the latitude allowed to experimental error. In order that it should fit that portion of the figure which Mr. Lupton said it did, the latitude to be allowed would have to be 10 to 100 times greater than that for which there was any warrant. This, he considered, was not allowable. The figures here referred to (and exhibited at the meeting) were the first differential figures (rate of change) deduced directly from the determinations themselves; the question, therefore, of the accuracy attainable in differentiating a graph, raised by Professor Ramsay, did not apply to them.

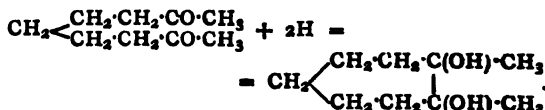
It seemed somewhat rash of Professor Armstrong to hold that a particular hydrate ($\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$) did not exist in solution at moderately high temperatures, because from a study of one property he had recognised it at low temperatures only, especially as it was from his own results at high temperatures that the speaker had been led to search for it, and finally to isolate it, at low temperatures. The multiplicity and complexity of the hydrates indicated must, no doubt, endanger the acceptance of his conclusions amongst chemists; but without reason, he thought, for we are at present in the dark as to the nature of liquid molecules (see *loc. cit.*, pp. 124, 129). He would be perfectly ready to accept any other explanation of the changes with weak solutions than that of their being due to hydrates, but he considered that we have at present no evidence in favour of any other view, or of their being due to changes in the aggregation of the solvent molecules, while the fact that they are precisely similar to the changes with strong solutions which occur at simple molecular proportions forces us to attribute them to the same cause as the latter, until some evidence to the contrary be forthcoming. He had already alluded to the question raised by Dr. Morley, as to why the existence of a hydrate should cause a change of curvature at exactly the strength of the solution corresponding to it (*loc. cit.*, p. 138), but he had left that question to those who had sufficient mathematical abilities to deal with it. Mendeléeff, however, appeared to consider that no exception could be taken on that score (*C. S. Trans.*, 1887, p. 779).

The fact mentioned by Prof. Rücker, that a flexible spring could be made to fit any complicated curvilinear figure by fixing it in position by a sufficient number of

pins, did not appear to disprove the existence of definite changes of curvature in the figure; for the forces acting on the spring between any two given pins would be different from those acting on it between any other two; and, consequently, the form of the different portions of the spring would be represented by different equations, that is, there would be changes of curvature. He did not see how the position of these changes of curvature could be said, on either theoretical or practical grounds, to depend on the flexibility of the spring used; for he believed he was correct in saying that all springs, when acted on by forces of a similar nature, assumed similar forms, and any difference in the degree of curvature due to a difference in flexibility might be counteracted by a difference in the magnitude of the forces applied. In practice, he had used numerous springs of very different degrees of flexibility, without finding any difference in the position of the changes of curvature indicated. It seemed scarcely correct to say that the application of a flexible lath to a curvilinear figure led to different results in different hands, because Mendeléeff's conclusions respecting the densities of sulphuric acid differed from the speaker's; for Mendeléeff had an altogether insufficient number of experimental points at his disposal, and, as far as could be judged, did not use a flexible lath at all in examining them. The question as to whether a lath could or could not be used in locating changes of curvature which were not apparent to unassisted inspection might be most easily settled by submitting a fictitious series of determinations, calculated from sundry different equations, to examination with a lath, and ascertaining whether the position of the changes of curvature found coincided with those at which the equations had been changed. He was quite ready to submit his process to this crucial test.

27. "Ethylic $\alpha\alpha'$ -Dimethyl- $\alpha\alpha'$ -Diacetylpimelate and its Decomposition Products." By F. STANLEY KIPPING, Ph.D., D.Sc., and J. E. MACKENZIE, B.Sc.

When diacetylpentane is reduced with sodium and moist ether it is converted into dimethyldihydroxyheptamethylene (*cf.* Kipping and Perkin, *Chem. Soc. Trans.*, lix., 214), according to the equation—



As it seemed probable that other 1:7-diketones would behave in a similar manner, the authors have prepared $\alpha\alpha'$ -dimethyl- $\alpha\alpha'$ -diacetylpentane by the method described below. The action of reducing agents on this diketone is now being investigated by one of them, but, as a considerable amount of work has yet to be done on the subject, they describe in the present paper the preparation and properties of dimethyldiacetylpentane and of various other compounds obtained in the course of the research.

Ethylic $\alpha\alpha'$ -dimethyl- $\alpha\alpha'$ -diacetylpimelate,



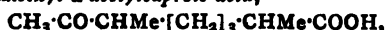
is formed in considerable quantities when ethylic sodium-methylacetate (2 mols.) is treated with trimethylene bromide (1 mol.) in absolute alcoholic solution; it is a colourless oil boiling at 233–235° under a pressure of 50 m.m., and it combines readily with phenylhydrazine (2 mols.), yielding a reddish-yellow *dihydrasone*, which has the composition $\text{C}_{25}\text{H}_{40}\text{N}_4\text{O}_4$. On boiling with alcoholic potash the ethereal salt is readily decomposed, the principal products being $\alpha\alpha'$ -dimethyl- $\alpha\alpha'$ -diacetylpentane, $\alpha\alpha'$ -dimethyl- α -acetylcaproic acid, and $\alpha\alpha'$ -dimethylpimelic acid.

$\alpha\alpha'$ -Dimethyl- $\alpha\alpha'$ -diacetylpentane,



is a colourless liquid boiling at 202–204° under a pressure of 150 m.m.; when treated with hydroxylamine it is converted into a crystalline *dioxime*, $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_2$, which melts at 93–94°.

aa'-Dimethyl-a-acetylcaproic acid,



is a colourless oil boiling at 226—228° under a pressure of 70 m.m., seemingly with slight decomposition. The *silver* salt, $\text{C}_{10}\text{H}_{17}\text{O}_4\text{Ag}$, *ethyl* salt, $\text{C}_{12}\text{H}_{22}\text{O}_4$, *methylic* salt, $\text{C}_{11}\text{H}_{20}\text{O}_4$, and the *hydroxime*, $\text{C}_{10}\text{H}_{19}\text{NO}_3$, are described.

aa'-Dimethylpimelic acid,



separates from light petroleum in well-defined crystals, melts at 80—81°, and is readily soluble in most ordinary solvents. The *silver* salt, $\text{C}_9\text{H}_{14}\text{O}_4\text{Ag}_2$, and the *barium* salt, $\text{C}_2\text{H}_{14}\text{O}_4\text{Ba}$, were prepared.

Ethyl-aa'-dimethylpimelate,



is formed in the place of ethyl dimethyldiacetylpmelate when trimethylene bromide is treated with ethyl sodio-methylacetoacetate in alcoholic solution, the alcohol employed being not quite anhydrous; it is a colourless oil boiling at 190—191°, under a pressure of 80 m.m.

28. "Volatile Platinum Compounds." By W. PULINGER.

At Prof. Lothar Meyer's suggestion, the author has further studied the volatile compounds of platinum with chlorine and carbon monoxide described by Schützenberger, with the object, if possible, of determining their vapour density. He describes their behaviour when heated in various gases, as they do not completely volatilise, even in carbonic oxide, he was unsuccessful in accomplishing his object.

In preparing the compounds, he has obtained a novel compound of the formula $\text{PtCl}_6\text{C}_2\text{O}_2$, as a non-volatile, yellow, crystalline solid, easily soluble in water, and recoverable apparently unchanged from the solution. Liquid carbonyl chloride at 100° is found to act as a solvent of Schützenberger's compounds, depositing them on cooling in large crystals.

The author has prepared the compound PtBr_2CO by heating platinous bromide in an atmosphere of carbonic oxide; apparently it is the only product even when excess of the gas is used. It crystallises in well-defined needles melting at 177°, and volatilising with extreme difficulty even in an atmosphere of carbonic oxide.

Directions are given for the preparation of platinum bromide and iodide, from which it appears that platinum sponge readily dissolves when merely boiled with either a solution of bromine in bromhydric acid or of iodine in iodyhydric acid.

DISCUSSION.

Dr. COLLIE mentioned, as an instance of a volatile metallic derivative, that he had recently had occasion to notice that the copper derivative of the double ketone diacetylmethane, $(\text{Ac}_2\text{CH})_2\text{Cu}$, was volatile.

PHYSICAL SOCIETY.

June 12th, 1891.

Prof. W. E. AYRTON, F.R.S., President, in the chair.

MR. W. H. DINES, B.A., was elected a member of the Society.

Prof. W. G. ADAMS then took the Chair, whilst Prof. AYRTON read a paper on "Alternate Current and Potential Difference Analogies in the Methods of Measuring Power," by himself and Dr. SUMPNER.

In a paper read before the Society in March last, the authors pointed out that for every method of measuring power in which readings of volts and amperes were taken, other methods in which amperes were read instead of volts, and volts instead of amperes, could be devised. More recently Dr. Fleming had, by a transformation of a formula given by the authors in a communication made to the Royal Society on the measurement of power by

three voltmeters, given the analogue in which three ammeters were employed. The two arrangements are represented in Figs. 1 and 2, whilst Fig. 3 shows a modification of Dr. Fleming's method (Fig. 2), in which the current in the non-inductive resistance, r , is measured by the aid of a voltmeter, V , across its terminals. This obviates the necessity of putting an electromagnet in what should be a non-inductive circuit. The

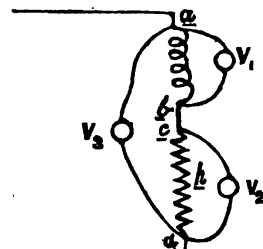


FIG. 1.

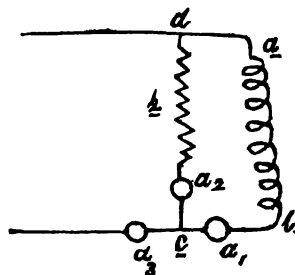


FIG. 2.

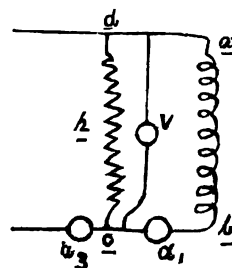


FIG. 3.

formula for the mean watts spent in the circuit $a b$, Figs 1 and 2, are respectively—

$$W = \frac{I}{2r} (V_2^2 - V_1^2 - V_3^2) \text{ and } W = \frac{r}{2} (A_2^2 - A_1^2 - A_3^2).$$

Mr. Blakesley's method of measuring power by a split dynamometer was shown to be analogous to the original electrometer method in which the difference of two readings was proportional to the power, and Blondlot and Currie's double electrometer method was shown to be the analogue of the ordinary wattmeter. The wattmeter was defective in the fact that a solenoidal coil was inserted in a nominally non-inductive circuit. The error thus introduced is, as was shown by one of the authors some years ago, expressed by the formula—

$$\frac{\text{Apparent watts}}{\text{True watts}} = \frac{1 + \tan \theta \tan \phi}{1 + \tan^2 \phi}$$

where θ is the phase angle between the current and E.M.F. in the circuit in which the power is to be measured, and ϕ the phase angle for the approximately non-inductive

circuit. It is now proved that the same formula expresses the error in any of the methods where resistances not wholly non-inductive are used.

As is well known, Mr. Blakesley has applied his split dynamometer to the measurement of phase differences between two currents; and an analogous method of finding the phase difference between two potential differences is described in the paper. In this method a high resistance split dynamometer, such as suggested by Mr. Rimington for measuring power, is employed. Blondlot and Currie's electrometer could also be used for the same purpose. Numerous diagrams illustrating the various analogies accompany the paper.

Prof. S. P. THOMPSON enquired whether hot-wire voltmeters could be employed to measure the various potential differences without introducing error.

In reply, Prof. AYRTON said that, although no great error was introduced by the self-induction of these instruments, yet the fact that they required considerable current was a disadvantage, and as these currents were not always in the same phase as those in other circuits, troublesome corrections were sometimes necessary. Electrostatic instruments were preferable.

Prof. ADAMS said he was glad to hear the inductance of Cardew voltmeters introduced no serious error, for they were very convenient instruments to use.

Prof. O. LODGE, F.R.S., exhibited *A Clock for Pointing Out the Direction of the Earth's Orbital Motion in the Ether*.

After mentioning the various motions to which a point on the earth's surface is subjected, he pointed out that the orbital motion was the largest component, and its direction at any instant not easy to conceive. An apparatus for pointing out this direction was therefore convenient when dealing with problems requiring a knowledge of the motion of a point through the ether. In one of two clocks shown, one spindle representing the earth's polar axis and another the axis of the ecliptic were inclined at an angle $23\frac{1}{2}^\circ$ and coupled by a Hooke's joint. The latter axis was capable of rotating round the former. At its upper end the ecliptic axis carried a tube and a pointer, both being perpendicular to the axis and to each other. The clock keeping solar time rotated both axes, and when properly set, the tube pointed in the direction of the sun, and the pointer therefore indicated the direction of the earth's orbital motion.

Some Experiments with Leyden Jars were then shown by Dr. LODGE.

The first one was with resonant jars, in which the discharge of one jar precipitated the overflow of another when the lengths of the jar circuits were properly adjusted or tuned. The latter jar was entirely disconnected from the former, and was influenced merely by electro-magnetic waves emanating from the discharging circuit. Lengthening or shortening either circuit prevented the overflow. Correct tuning was, he said, of great importance in these experiments, for a dozen or more oscillations occurred before the discharge ceased. The effect could be shown over considerable distances. In connection with this subject, Mr. Blakesley had called his attention to an observation made by Priestley many years ago, who noticed that when several jars were being charged from the same prime conductor, if one of them discharged, the others would sometimes also discharge, although they were not fully charged. This he (Dr. Lodge) thought might be due to the same kind of influence which he had just shown to exist. The word *Resonance*, he said, was often misunderstood by supposing it always had reference to sound, and, as substitutes, he thought that *sympsoning* or *sympsonic* might be allowable.

The next experiment was to show that wires might be tuned to respond to the oscillation of a jar discharge just as a string could be tuned to respond to a tuning fork. A thin stretched wire was connected to the knob of a jar, and another parallel one to its outer coating, and by vary-

ing the length of an independent discharging circuit, a glow was caused to appear along the remote halves of the stretched wires at each discharge; each of the wires thus acted like a stopped organ pipe, the remote ends being the nodes at which the variations of pressure are greatest. By using long wires he had observed a glow on portions of them with the intermediate parts dark; this corresponded with the first harmonic, and by measuring the distance between two nodes he had determined the wave-length of the oscillations. The length so found did not agree very closely with the calculated length, and the discrepancy he thought due to the specific inductive capacity of the glass not being the same for such rapidly alternating pressures as for steady ones. He also showed that the electric pulses passing along a wire could be caused, by tuning, to react on the jar to which it was connected and cause it to overflow even when the distance from the outside to the inside coating was about eight inches. During this experiment he pointed out that the noise of the spark was greatly reduced by increasing the length of the discharging circuit. The same fact was also illustrated by causing two jars to discharge into each other, spark gaps being put both between their inner and outer coatings, so as to obtain "A" sparks and "B" sparks. By putting on a long "alternative path" as a shunt to the "B" spark gap, and increasing that gap, the noise of the "A" spark was greatly reduced. He had reason to believe that the "B" spark was a quarter phase behind the "A" spark, but the experimental proof had not been completed.

He next described some experiments on the screening of electromagnetic radiation, in which a Hertz resonator was surrounded by different materials. He had found no trace of opacity in insulators, but the thinnest film of metal procurable completely screened the resonator. Cardboard rubbed with plumbago also acted like a nearly perfect screen. In connection with resonators he exhibited what he called a *graduated electric eye* or an *electric harp* made by his assistant, Mr. Robinson, in which strips of tin-foil of different lengths are attached to a glass plate, and have spark gaps at each end which separate them from other pieces of foil. One or other of the strips would respond according to the frequency of the electromagnetic radiation falling upon it.

Mr. BLAKESLEY asked whether the tuning of the resonant jars needed re-adjustment when the distance between their circuits was varied, for, according to theory, the mutual induction should diminish the self-induction of the primary, and cause its oscillations to be more rapid. If this was true the method might be used for getting rapid oscillations. He also inquired whether the glow would appear in the same position on the two stretched wires if their ends were joined.

Dr. SUMPNER wished to know how the resistances, inductances, and capacities of the circuits and jars were determined, and whether any evidence of irregular distribution of the charges on the tin-foil had been noted. With reference to the overflowing of a jar caused by using a certain length of discharging circuit, he asked whether the overflow did not prove the existence of a higher potential than that which originally existed between the coatings of the jar, and, if so, where did the excess energy come from?

Dr. THOMPSON asked if it would be possible to make a wire circuit analogous to an open organ pipe by putting sheets of metal on the ends of the wires.

Dr. LODGE, in reply, said Mr. Blakesley's suggestion was an important one, but he had not observed that any change in the adjustment was necessitated by varying the distance between the resonating circuits. Neither had he noticed any glow on wires joined to form a single loop, but this might be possible if the wires were long enough to give harmonics.

In answer to Dr. Sumpner, he said that the capacities were difficult to determine, for with much rapid oscillations the coatings were virtually enlarged. Lord Rayleigh

had shown how to calculate the inducances, and the resistances he had practically measured by his alternative path experiments. The overflow of jars he thought was caused by the charges in some way concentrating on the edges of the foil, thus causing a kind of flood tide at which the overflow occurred.

The PRESIDENT asked Dr. Lodge what his views were as to the cause of the opacity of ebonite to light. Was it due to a selective absorption which cut off only the rays to which the eye was sensitive, or was the ordinary explanation that it contained impurities which were conducting and hence acted as screens likely to be correct? Another possible explanation was that the motion of the ether particles may be in three dimensions, and light be due to the projection of this motion on a plane perpendicular to the ray, whilst electro-magnetic induction might be due to the other component.

Dr. LODGE said he believed that ebonite was not opaque because of conducting particles being present, and was inclined to think that it acted more like ground glass, in which the opacity was due to internal reflections. Such a substance would only be opaque to vibrations whose wave-lengths were comparable with the size of the particles.

A Note "On the Construction of Non-Inductive Resistances," by Prof. W. E. Ayrton, F.R.S., and Mr. T. Mather, was postponed until next meeting.

CORRESPONDENCE.

THE RELATION BETWEEN THE CHEMICAL CONSTITUTION OF CERTAIN ORGANIC COMPOUNDS AND THEIR ACTION UPON THE ULTRA-VIOLET RAYS. (A CORRECTION).

To the Editor of the Chemical News.

SIR,—Having carefully perused the communications of Dr. Gerhard Krüss, which are of particular interest to me, I remark that in his paper entitled "Beziehungen Zwischen Zusammensetzung und Absorption-Spektrum organischer Verbindungen" (*Zeits. für Physikalischen Chemie*, vol. ii., p. 312) he very properly refers to papers on the subject by MM. Soret and Rilliet, *Comp. Rend.*, lxxxix., 747 (1879), and of J. L. Schön, *Ann. Phys.* (2), vi., 267; but he has attributed the original work of Prof. Huntington and myself to Mr. W. R. Dunstan, who has merely made use of abstracts of the following papers by us:—(1) "Researches on the Action of Organic Substances on the Ultra-Violet Rays of the Spectrum." Parts I. and II. (*Phil. Trans.*, 170, p. 257, Part I., 1879); and (2) "Researches on the Action of Organic Substances on the Ultra-Violet Rays of the Spectrum," Part III.; "An Examination of Essential Oils" (*Proc. Roy. Soc.*, xxxi., p. 1, 1880). Also (3) the memoirs by myself entitled "Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra" (*Journ. Chem. Soc.*, xxxix., p. 153, Parts I. to V., 1881). These communications were read on June 3rd and December 2nd, 1880. My later investigations, published under the same general title, in 1882, 1885, and 1887, are not mentioned, and have probably been overlooked by Dr. Krüss, though the last communication (Part VIII., *J. Chem. Soc.*, 51), "A Study of Coloured Substances and Dyes," deals with the effect of NH_2 and OH groups in the molecules of such substances upon the absorption spectrum. I do not desire to draw attention to any accidental omission on the part of Dr. Krüss, but rather to point out the inconvenience to authors which may arise from the publication of communications such as that which Prof. Dunstan prepared. It is headed "Report on Organic Chemistry," to which is

given the specific title "The Relation between the Chemical Constitution of certain Organic Compounds and their Action upon the Ultra-Violet Rays."

Owing to the manner in which this Report is reproduced in the *Pharmaceutical Journal* (xi., p. 54, 1881) it is by no means evident that the matter contained therein is not original. In point of fact it reads as if the deductions were drawn by Prof. Dunstan, after a study of our memoirs in the *Phil. Trans.*, *Proc. Roy. Soc.*, and *Journ. Chem. Soc.*

Dr. Krüss thus appears to have been misled into attributing the authorship of the above-mentioned work to the author of the title only. By this Report being quoted and referred to as an original contribution I also was misled, and put to the trouble of consulting it. I then found that it was published actually prior to my papers entitled "Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra," for, although they had been verbally communicated to the Chemical Society as early as June 3rd, 1880, and in writing on December 2nd of the same year, they were of necessity not published in the *Journal* until March, 1881, while Prof. Dunstan's Report upon them appeared in January. He thus appears to be entitled to priority in respect of these matters, and I am under the necessity of requesting you to be so good as to allow me to make this correction.—I am, &c.,

W. N. HARTLEY.

Royal College of Science for Ireland,
Stephen's Green, Dublin, June 5, 1891.

EXAMINATIONISM.

To the Editor of the Chemical News.

SIR,—The latest edition of the Directory issued by the Department of Science and Art of the Committee of Council on Education contains the following section relating to the quantitative portion of the Honours Stage Examination in Practical Inorganic Chemistry (Subject X.p.):—"II.—A practical examination in quantitative analysis, in which the candidate will have to make a quantitative determination of one of the following bodies: lead, silver, iron, calcium, potassium, ammonium, hydrochloric acid, sulphuric acid, carbonic acid."

At the examination on May 30th last, the exercise set in quantitative analysis was an alloy containing copper, the percentage of which was to be determined gravimetrically.

There is, I am aware, much to be said for and against examinational tests of capability; but there can scarcely be two opinions as to the unfairness of issuing a definitively worded syllabus, and then setting, or permitting to be set, an exercise absolutely outside it. Why issue the syllabus at all? In a case within my own immediate observation, a candidate who (if the syllabus had been adhered to) would certainly, as far as could be foreseen, have obtained a first-class, was so taken aback by having an alloy set before him composed of metals not included in the list published for his guidance that he omitted the quantitative portion of the examination altogether, although I believe he performed the qualitative work very well, and know that he could have accurately made any of the quantitative estimations provided for in the syllabus. What the results in his own case may be I do not know but there must have been many similar cases. No doubt it may be said, in deprecation of criticism, that the exercise set was easy, and that with the directions given (which, by the way, were not complete), the candidates' knowledge of quantitative manipulation should have been sufficient to carry them through. This, I submit, would be no defence: the point being whether the detailed syllabus should or should not, in fairness, have been adhered to.

I see that this matter has already called forth some strong remarks from the lynx-eyed editor of *Truth*, but

as I have observed no reference to the subject in the scientific journals to which I have had access I venture to trouble you with this letter.—I am, &c.,

E. GODWIN CLAYTON, F.I.C., &c.

Chemical Laboratory,
43 and 44, Holborn Viaduct, London, E.C.,
June 16, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxii., No. 23, June 8, 1891.

Action of Ammonia upon certain Compounds of the Halogen Salts of Mercury.—M. Raoul Varet.—The author has examined the action of aqueous ammonia upon the compounds of mercury iodide with the cyanides. He has particularly studied the double mercury and cadmium iodicocyanide; the mercury and potassium iodicocyanide, a salt which dissolves in aqueous ammonia, heated to about 40°, is deposited again on cooling, without having fixed any ammonia. Gaseous ammonia is taken up by mercury cyanide with difficulty, forming a white amorphous body, HgCy.NH_3 , which rapidly loses ammonia if exposed to the air and absorbs water, which may be again expelled by re-treatment with a current of NH_3 . Mercury and barium chlorocyanide takes up 3 equivalents NH_3 , if treated with a current of gaseous ammonia at 100° until completely dehydrated and then for 8 hours longer in the cold.

A New Method of Preparing Silicon Chloroiodides.—A. Besson.—The three chloroiodides which are theoretically possible are easily obtained by allowing chlorine and silicon iodide to act upon each other simultaneously in the nascent state.

Revue Générale des Sciences Pures et Appliquées.
Vol. ii., No. 8, March 15, 1891.

Chemical Equilibria. Part Second. Application of the Principles of Thermodynamics.—H. Le Chatelier and G. Mouret.—The authors announce the following general laws as governing the transformation of all chemical systems whatsoever:—

1. The chemical transformation effected at fixed tensions without the intervention of foreign energies other than those exchanged with the medium is that which answers to a decrease of potential, a quantity expressed by the formula $\pi = u - st + vp$, where u , s and v are the internal energy, the entropy, and the volume of the system, t and p are the temperature and the pressure of this medium.

2. In order that a chemical system may be in equilibrium, it is necessary and sufficient that the potential is maximum, minimum, or constant.

3. When the tensions of dissociation vary from dp and dt the transformation effected is that for which the utilisable chemical energy is positive, i.e., that for which we have the relation—

$$L \frac{dt}{t} + N \frac{dp}{p} > 0,$$

where L and N are the energies of chemical transformation, latent heat, and work, p and t are the tensions.

4. In order that there may be isodissociation, i.e., in order that the simultaneous variations of the tensions of dissociation may not modify the chemical state of the

system supposed free from any connection, the variations must satisfy the relation—

$$L \frac{dt}{t} + N \frac{dp}{p} = 0.$$

5. In order that a chemical system which is homogeneous, or has fixed tensions, may be in equilibrium it is necessary and sufficient that the potentials of its elements referred to the unit of mass may be equal.

Revue Universelle des Mines et de la Metallurgie.

Vol. xiii., No. 3.

This issue does not contain any chemical matter.

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NOTE ON SOME OBJECTIONS TO THE WORK ON SULPHURIC ACID SOLUTIONS.

By SPENCER U. PICKERING, F.R.S.

THE importance of the discussion which took place at the Chemical Society on June 4th (*CHEMICAL NEWS*, lxxiii., 305), on the subject of the hydrate theory of solution, and on my method of examining series of experiments, must be my excuse for answering some of the objections which were raised, and which my already published answer does not adequately meet.

It is scarcely necessary, perhaps, to point out that Prof. Armstrong is quite in error when he interprets the 102 breaks in the figures representing various properties of sulphuric acid solutions as meaning the existence of 102 *different* hydrates, for the same hydrate will account for as many breaks as there were properties examined. The actual number of hydrates of which I found indications in the case in question was only twenty, and I must again protest against the unscientific nature of any objection to their existence on the grounds that their number is greater than we might expect; for we have no right to expect anything at all, being at present entirely in ignorance of the nature or number of those loosely combined and partially dissociated compounds which can exist in the liquid condition.

It is certainly surprising to find Prof. Armstrong producing as a novel discovery, and as the result of his own experience, the conclusion that "changes of composition" (? constitution), "whenever they occurred, were indicated on the curves drawn directly to represent the experimental results"; for this is the very point on which I have insisted all along. Before I had published any of my experimental results, I said (*Nature*, 1889, p. 343), "Differentiation will sometimes bring about the recognition of breaks which might be overlooked in the original curve, for, though the differential curve can show no breaks which do not exist in the original curve, it may often, as a consequence of its very nature" (*i.e.*, being more nearly rectilinear than the original curve), "show breaks clearly which would be recognised only with difficulty in the original curve"; while at the commencement of my first paper on Sulphuric Acid (*Chem. Soc. Trans.*, 1890, p. 68) I said, "I would, with the experience I have gained, generally trust as much to the drawing of the original curve as to differentiation, for showing whether that curve is continuous or not, and where the changes occur in it." In my second paper on Sulphuric Acid I used differentiation to a limited extent only, and as affording supplementary evidence to that derived from a study of the experimental curves (*Chem. Soc. Trans.*, 1890, p. 345); while in all the work of this nature which I have done

during the last eighteen months I have not used differentiation once (see *B. A. Report*, 1890, 312, and *CHEM. NEWS*, lxxii., 185), although there are undoubtedly some advantages to be obtained through its proper use. Thus Professor Armstrong's experience on this point agrees entirely with my own; so also does Professor Rücker's, though I think that there must be some mistake about his statement that it was a study of my density results which led him to this conclusion, for the original density curve cannot, as a matter of fact, be plotted out at all on any workable scale.

The fact that, in my paper on Sulphuric Acid, I gave a list of the scales which I had found most suitable for plotting out my results seems to have led Prof. Rücker to conclude that the position of the breaks may be made to vary with the scale used. This is certainly not the case (although of course we can select a scale so badly proportioned that it would be utterly useless). I mentioned in my paper (p. 68) that "Drawings on several different scales, and with several different points as origins, were made in all cases, and the labour entailed in the treatment of the results has by far exceeded that of the determinations themselves."

Prof. Rücker's conclusion, that any break which is recognised only in the differential figure deduced from the experimental figure, and not in the experimental figure itself, is "of the most untrustworthy character," is precisely my own conclusion. In the two or three instances in which such indications were obtained I regarded them merely as suggestions (see p. 77 of my paper), and in no single instance did I accept them alone as proving the existence of a hydrate.

Prof. Rücker says that the fact that a series of results may be represented more closely by two curves than by one, may not imply a discontinuity, *because*, by admitting a sufficient number of discontinuities, the results may be represented graphically with absolute fidelity. I certainly fail to see the force of this argument. A drawing which represents experimental results as being entirely free from experimental error is obviously incorrect, and the mere fact that it is physically possible to make an illegitimate drawing of this sort does not throw any discredit on other drawings which are in harmony with the ascertained magnitude of the experimental error. The problem of the correct depiction of results graphically is not a very difficult one; we must adopt the simplest drawing which is consistent with the known experimental error, and discard any drawing which attributes an error to the experiments, either greatly in excess or greatly below that of the observed or probable experimental error. As an instance I may take the diagram which was exhibited at the meeting of the Chemical Society, and which will be found in the July number of the *Phil. Mag.* (xxxii., 94), in my

answer to Mr. Lupton's criticism. It consists of eleven experimental points representing the rate of change of the density with change of composition, and the question is whether these results should be represented by 5 (the greatest possible number), 4, 3, 2, or 1 curves. The safe limit to be assigned to the experimental error is 0.000008 (*Chem. Soc. Trans.*, 1890, p. 71), and depicting these results by—

5	4	3	2	1 curves,
we get—				
0	0.000003	0.000008	0.000007	0.000078

as the apparent error of the points. Drawn as 5 or 4 curves, this apparent error would be too far below the experimental error; the 3 curve drawing is legitimate as far as the magnitude of the error is concerned, but, as we can simplify the drawing still further without any increase—indeed with a slight decrease—of the apparent error, we are bound to make this simplification, and to accept the 2 curve drawing in preference to the 3 curve drawing. But no further simplification is possible; for simplifying it one degree further produces a sudden tenfold increase in the apparent error, and makes this ten times greater than the ascertained experimental error. Thus the 2 curve drawing is the simplest, and the only possible representation.

Dr. Morley's objection is, I think, a mistaken one. A break at a particular hydrate by no means implies that this particular hydrate has only just begun to form there. Supposing there to be three hydrates: CaCl_2 with 7, 8, and 9 H_2O respectively; then, as water is added to $\text{CaCl}_2 \cdot 7\text{H}_2\text{O}$, its effect will be to form some of the $\text{CaCl}_2 \cdot 8\text{H}_2\text{O}$, and, as more water is added, the relative proportion of $\text{CaCl}_2 \cdot 8\text{H}_2\text{O}$ present will be increased: as soon, however, as more water is added than is necessary to entirely form the $\text{CaCl}_2 \cdot 8\text{H}_2\text{O}$, another hydrate, $\text{CaCl}_2 \cdot 9\text{H}_2\text{O}$, will begin to make its appearance, and the effect of adding more water now will be to increase the relative proportion of the latter and diminish the relative proportion of the $\text{CaCl}_2 \cdot 8\text{H}_2\text{O}$ present: thus the effect of adding water to solutions stronger than $\text{CaCl}_2 \cdot 8\text{H}_2\text{O}$ will be different to that produced by adding it to solutions weaker than $\text{CaCl}_2 \cdot 8\text{H}_2\text{O}$; in other words, there will be a change in the rate of the effect at the composition of the $\text{CaCl}_2 \cdot 8\text{H}_2\text{O}$ itself: this is just what is actually observed

AN APPARATUS FOR TESTING THE SENSITIVENESS OF SAFETY-LAMPS.*

By FRANK CLOWES, D.Sc., Lond.,
Professor of Chemistry, University College, Nottingham.

It is generally acknowledged that the Davy safety-lamp cannot with certainty detect less than 3 per cent of firedamp in the air of the mine. Gas-indicators of much greater sensitiveness have been invented; amongst these the electrical apparatus of Liveing and the spirit safety-lamp of Pieler take first rank. The objection to these special forms is, however, a serious one. They do not serve for illuminating purposes, and therefore it becomes necessary to carry an ordinary safety-lamp together with the testing apparatus. Many attempts have been made to obviate this inconvenience by producing a safety-lamp which shall serve the double purpose of illumination and of detecting minute percentages of firedamp. The discovery of such a lamp would be of great value to the miner, in view of the fact that very low percentages of firedamp have been proved to be dangerous in the presence of coal-dust.

The following apparatus has been devised to render easy the process of testing the sensitiveness of different forms of safety-lamps when used for detecting firedamp.

To enable satisfactory tests to be made in the laboratory, it was necessary to insure (1) the easy and rapid production of mixtures of firedamp and air in known proportions; (2) to insure economy of the artificially prepared methane, which represented firedamp; and (3) to examine the flame of the lamp under conditions as satisfactory as those existing in the mine.

A wooden cubical box of about 100 litres capacity, was constructed so as to be as nearly gas-tight as possible. It was then made absolutely gas-tight by painting it over with melted paraffin wax, which was afterwards caused to penetrate more perfectly by passing an ordinary hot flat-iron over the surface. This testing chamber was furnished with a small inlet tube at the top, and with a similar outlet tube below. It had a plate glass window in front for observing the lamp in the interior, and a flanged opening below for introducing the safety-lamp. This opening was closed by a water-seal consisting of a small zinc tray supported by buttons, and containing about two inches depth of water, into which the flange dipped. A mixer was arranged, which consisted of a light flat board, nearly equal in dimensions to the section of the chamber, and suspended by an axis from the upper corner of the chamber. The mixer was moved rapidly backwards and forwards from the side to the top of the interior of the chamber, by grasping a handle projecting through the front of the chamber.

When a mixture of air with a certain definite percentage of firedamp was required, the methane, prepared and purified by ordinary chemical methods, was introduced into the chamber in the requisite quantity by the top inlet. It displaced an equal volume of air which escaped through the lower outlet, the exit end of which was sealed by being immersed just beneath a water surface. A vigorous use of the mixer secured a uniform mixture of gas and air throughout the interior of the chamber in the course of a few seconds. The lamp was then introduced into the chamber, and placed in position behind the glass window. The simplicity of arrangement of the water-seal rendered the necessary opening of the chamber very brief, and the introduction and removal of the lamp many times in succession was not found to produce any appreciable effect upon the composition of the atmosphere inside the chamber. The appearance and dimensions of the "cap" over the flame were noted as soon as the cap underwent no further change. A lamp was left burning in the chamber for a considerable length of time, and its indications underwent no change owing to the large capacity of the chamber and the very limited amount of air required to support the combustion of the small flame always used in gas-testing. The whole interior of the chamber and mixer were painted dead black, so as to render visible pale and small caps against a black ground.

The methane was introduced from an ordinary gas-holder. A volume of water, equal to that of the methane to be displaced, was poured into the top of the gas-holder. The gas tap of the holder was then momentarily opened so as to produce equilibrium of pressure between the methane and the atmosphere. The gas tap having then been placed in connection with the upper inlet of the chamber, the water tap was opened and the measured volume of water was allowed to flow down and drive the methane into the chamber. As soon as bubbles of air ceased to appear through the water at the outlet, the chamber was closed; the mixer was then vigorously worked for a few seconds, and the mixture of gas and air was ready for the introduction of the lamp. Before introducing the methane for a fresh mixture, the atmosphere of the chamber was replaced by fresh air by removing the water-tray from beneath the opening at the bottom of the chamber, and blowing in a powerful stream of air from a bellows to the top of the chamber.

The chamber was supported on legs, which were arranged so as to place it at a convenient height for

* A Paper read before the Royal Society, June 18, 1891.

observations through the window, and also for the introduction and removal of the safety-lamp.

The accuracy of this method was tested by introducing the Pieler lamp into the chamber, which was charged successively with a series of mixtures containing proportions of methane varying from 0.5 to 4 per cent. The height and appearance of the cap over the flame absolutely corresponded with a series of standard tests already published and made by a different method in which fire-damp was used instead of methane.

The observations were usually made in a darkened room, but the flame caps were easily seen in a lighted room, provided direct light falling on the eye or chamber was avoided.

The capacity of the chamber was 95,220 c.c.; accordingly the following volumes of methane were introduced:—for 1 per cent mixture 476 c.c., for 1 per cent 952 c.c., for 2 per cent 1904 c.c., for 3 per cent 2856 c.c., for 4 per cent 3808 c.c., and for 5 per cent 4760 c.c. It will be seen that a series of tests, in which the above mentioned percentage mixtures were employed, involves an expenditure of only 15 litres of methane, a quantity far smaller than that required by any other method of testing as yet described.

Of many forms of safety-lamp tested in the above apparatus, the one which most satisfactorily fulfilled the two purposes of efficient illumination and delicacy in gas testing was Ashworth's improved Hepplewhite-Gray lamp. This lamp is of special construction, burns benzoline from a sponge reservoir, and its flame is surrounded with a glass cylinder, which is ground rough at the hinder part; this latter device prevents the numerous reflected images of the flame, and the generally diffused reflections which are seen from a smooth glass surface, and which render the observation of a small pale flame cap very difficult, if not impossible.

The wick of this lamp, when at a normal height, furnishes a flame of great illuminating power. When lowered by a fine screw adjustment the flame becomes blue and non-luminous, and does not interfere therefore with the easy observation of a pale cap. The following heights of flame cap were observed, which fully bear out the unusual sensitiveness of this flame. With 0.5 per cent of methane 7 m.m.; with 1 per cent 10 m.m.; with 2 per cent 14 m.m.; with 3 per cent 20 m.m.; with 4 per cent 25 m.m.; and with 5 per cent 30 m.m. The cap, which with the lower proportions was somewhat ill-defined, became remarkably sharp and definite when 3 per cent and upwards of methane was present. But even the lowest percentage gave a cap easily seen by an inexperienced observer.

It appears from the above record of tests that the problem of producing a lamp which shall serve both for efficient illuminating and for delicate gas testing purposes has been solved. The solution is in some measure due to the substitution of benzoline for oil, since the flame of an oil flame cannot be altogether deprived of its yellow luminous tip without serious risk of total extinction, and this faint luminosity is sufficient to prevent pale caps from being seen.

From further experiments made in the above testing chamber with flames produced by alcohol and by hydrogen it was found to be true in practice, as might be inferred from theory, that if the flame was pale and practically non-luminous, the size and definition of the flame cap was augmented by increasing either the size or the temperature of the flame. It is quite possible by attending to these conditions to obtain a flame which, although it is very sensitive for low percentages of gas, becomes unsuitable for the measurement of any proportion of gas exceeding 3 per cent. This must, for the general purposes of the miner, be looked upon as a defect; but it is not a fault of the lamp already referred to. It is of interest to note that with the Pieler spirit lamp a flame cap an inch in height was seen in air containing only 0.5 per cent of methane.

PURIFICATION OF CHEMICALS BY EXPOSURE TO INTENSE COLD.

By H. THOMS.

THE author was informed by Pi&et, who has taken out a patent for the process, that from the purest chloroform of commerce, if cooled down to about -70° , there separated out a crystalline body, which is then drained from the part which remains liquid. This liquid portion is then exposed to a temperature below -100° , when the chloroform itself crystallises out, and can be separated from an impurity which remains liquid.

Chloroform purified in this manner is a colourless liquid, having at 15° the sp. gr. 1.51. It is in course of an investigation by O. Liebrich. It is indefinitely permanent on exposure to light. Whilst the so-called pure chloroform of commerce takes a greenish colour if shaken up with solution of potassium dichromate and sulphuric acid, if Pi&et's chloroform is similarly treated the chromic mixture retains its yellowish colour. — *Chemiker Zeitung and Pharm. Central-Halle.*

THE BABCOCK METHOD FOR ESTIMATING THE FAT IN MILK.

By FRANK T. SHUTT, M.A., F.I.C., F.C.S.

PAYMENT of money according to value received is a sound principle recognised and acted upon as far as possible in every branch of commerce. With a view towards its application in the buying and selling of milk, it is necessary to know at the outset the elements in the composition of milk that determine the value of the latter for use in creameries and cheese factories, and, secondly, to apply some method whereby those valuable elements may be easily and cheaply determined.

The true commercial value of a milk depends upon its solid constituents. The variation in the total amount and composition of these constituents that exists between samples of genuine milk (due to food, breed, and individual characteristics), and the extreme ease with which water may be added to or cream abstracted from pure milk without detection by the unaided senses, make it highly desirable that there should be some rapid and accurate means, capable of being used by intelligent labour, for ascertaining within small limits the amount of such solids. The butter fat is so much the more important and valuable constituent in the solids that the knowledge of its percentage in a milk not only protects the buyer from fraud, but at the same time renders it possible for the seller to be paid according to the quality as well as the quantity of his milk—a plan that will commend itself as an equitable and satisfactory one to both parties.

The Babcock Method.

The usual methods of chemical analysis, while giving exceedingly accurate results, are lengthy, and must be conducted by experts in properly equipped laboratories. Numerous processes, however, have been devised of late by which the fat may be determined with a greater or less degree of accuracy in the creamery or factory. Such processes may be worked by the man in charge, and require but little time.

Prominent among these methods is the Babcock Test, which has for its principle the holding in solution of the solids other than fat by means of sulphuric acid, the fat at the same time separating as an oily layer. By the addition of water and the aid of centrifugal motion, the latter is brought into the graduated neck of the vessel in which the test is made and its amount at once noted. It is the object of the present report to bring before the farmers and dairymen of the Dominion our experience in the laboratories of the experimental farm regarding the

reliability and accuracy of this process for examining milk.

Examination as to Reliability and Accuracy.

Thirty-two samples of milk have been examined in duplicate by (1) the Babcock test, and (2) by gravimetric analysis, the results by the latter being taken, for the sake of comparison, as correct. These operations gave us 128 independent fat determinations.

As the results obtained throughout the whole series are uniformly close, it will suffice to tabulate here a few of them as examples:—

Milks: "Morning," "Evening," and "Mixed."

No.	Percentage of Fat by Babcock Method.	Percentage of Fat by Gravimetric Analysis.
1	4.4	4.54
	4.4	4.56
2	3.4	3.58
	3.5	3.56
3	3.6	3.72
	3.5	3.76
4	4.8	4.90
	4.8	4.91
5	5.8	6.04
	5.9	6.07
6	3.5	3.40
	3.3	3.35
7	3.4	3.60
	3.5	3.62
8	3.8	3.68
	3.7	3.68
9	3.8	3.87
	3.9	3.88
10	4.0	4.04
	4.0	4.03
11	3.3	3.32
	3.3	3.33
12	3.5	3.70
	3.7	3.69

An inspection of this table will reveal (1) the limits within which the amount of fat will vary when the Babcock test is made in duplicate, and (2) the approximation of such results to those given by carefully conducted chemical analyses.

Of the thirty-two samples tested in duplicate by the Babcock method, only two gave a difference between their duplicates amounting to three-tenths (0.3) of 1 per cent; two varied in their duplicates two-tenths (0.2) of 1 per cent; fourteen differed to the extent of one-tenth (0.1) of 1 per cent; and thirteen gave results identically the same.*

The greatest difference between fat determinations by the Babcock test and gravimetric analysis on the same milk was (0.25) a quarter of 1 per cent. This occurs in three instances only. Where the results are not identical the variation is usually between one-tenth and two-tenths of 1 per cent.

Conclusions.

From these data therefore we may safely conclude that when the Babcock test is made according to the instruction given with the machine, *strictly reliable results are obtained*, and that the percentage of fat so found, allowing for the greatest error possible under such circumstances, will be well within one-quarter of 1 per cent (0.25) of the amount of fat actually contained in the milk.

Recommendations.

Full instructions for operating the Babcock tester accompany each machine. Our own experience, however, leads me here to emphasize one or two particulars, the

* Since the above was done the Babcock tester has been in constant use for examining the milks produced at the farm. The samples have been tested in duplicate, and the results so obtained show no greater variation than those recorded above.

knowledge of which will assist in obtaining satisfactory results.

1. The milk should be well sampled. If the sample has stood several hours it should be thoroughly, though not violently, shaken before the pipette full is taken out. By this means any cream that has risen is once more uniformly suspended throughout the milk.

2. When a number of tests are to be made the milk of all the samples should be first carefully measured out into the bottles, the acid being added afterwards. When this is completed the two should be *thoroughly* mixed by shaking the bottle in the hand with a rotatory motion. The bottle should then be placed in the machine, which, when all the samples are placed, is immediately set in motion as directed. The thorough mixture of the acid and the milk tends to prevent the formation of curd or scum, which would interfere with the correct reading of the percentage of fat later on. If the bottles are whirled while still hot from the action of the acid, the fat separates more easily and quickly.

3. When the water is added, care should be taken that it is hot. No error can be made by having it too hot.

4. Hot water should also be placed in the machine so that the temperature of the mixture be not allowed to fall.

5. The amount of fat should be noted immediately at the close of the operation, and before the fat has had time to contract through loss of heat.

ON THE AMMONIA-SODA PROCESS.

By H. SCHREIB.

In the year 1876 appeared a report on a proposal of Mr. Thorwald Schmidt respecting the ammonia-soda process. Mr. Schmidt proposes to decompose the liquor of the ammonia-soda process containing chlorides of sodium and calcium, by a solution of the ashes of seaweed. The sulphates of potash, soda, and magnesia contained in the ash of the seaweed are decomposed so far that hydrated sulphate of lime and hydrated magnesia are precipitated in a form which may be available for paper making, as "pearl hardening."

By further adding certain admixtures to the said liquor, at last a pure solution of chloride of sodium is obtained, while, at the same time, iodine, nitrate, and iodides are produced.

The latter solution is then treated again by the ordinary ammonia-soda process for the production of bicarbonate of soda and white alkali. The proposal of Mr. Thorwald Schmidt cannot be generally used, as the ash of seaweed is not to be had everywhere, not to count for the somewhat circumstantial way of proceeding. But the method is based upon a sound idea, viz., the permanent regeneration of the liquor by simultaneously producing useful materials.

I have become induced, by the article of Mr. Schmidt, to introduce to your readers another proceeding practically confirmed for a number of years.

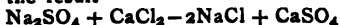
My way of treating the ammonia process is, as far as I know, the only one which has been applied hitherto to practically realise the products out of the said liquor, though I must, however, remark that I have been favoured by special opportunities, and that my idea of treating may scarcely be generally adopted.

A very large German manufactory, making an indispensable article for household consumption, possesses as auxiliary annex a small factory, producing per annum about 1000 tons of ammonia-soda required for the main works. The establishment in question requires, as well, large quantities of cardboard for packing purposes. This latter material, being of a cheap and grey-coloured quality, is also prepared by the same works in quantities of about 10 tons daily.

Owing to its unattractive appearance the cardboard is

to be painted. I had consequently suggested to produce the required "pearl hardening" (i.e., precipitated sulphate of calcium) out of the liquor of the ammonia process, in a way analogous to the one proposed by Mr. Thorwald Schmidt. But this could be done merely by adding sulphuric acid or sulphates.

When decomposing the liquid containing chloride of calcium and chloride of sodium by sulphate of sodium, (Na_2SO_4), the result—



will easily be obtained. The latter one is precipitated in connexion with two molecules of crystal water, and thus forms the wanted "pearl hardening." Besides, there remains a solution of chloride of sodium which may be very well used again for the ordinary ammonia process after it has become somewhat concentrated by boiling. But, however, this course of operating has not been taken by the works in question; for the manufactory wanted to prepare, if possible, also hydrochloric acid, of which it had need in rather large quantities.

The shortest way to aim at the desired result was to decompose the liquor of the ammonia process by sulphuric acid. The "pearl hardening" was thus precipitated, and an aqueous solution of hydrochloric acid originated therefrom. There is some common salt remaining in the solution too, but this is insignificant, and does not hinder the said proceeding.

The sulphuric acid employed for some years has now become replaced by acid sulphate of sodium, NaHSO_4 , owing to the comparatively cheaper price of the latter article.

The weekly production of "pearl hardening," used exclusively for painting the cardboard, amounts to about 30 tons. This way of painting is a highly elaborate one, for it gives to the cardboard a brilliant gloss after it has been salined so far that any lithographic produce may be printed directly upon the cardboard.

Nevertheless, it must be borne in mind that every manufactory will not be able to make the above-described advantageous use of the liquor out of the ammonia process.

A similar proceeding may, notwithstanding, be adopted in general, provided the works will be able to combine the production of hydrochloric acid with the preparation of sulphate, viz., the first part of the soda manufacturing according to Le Blanc's method with the ammonia process. The hydrochloric acid would then be saleable as usual, whilst the sulphate of sodium would be left for the decomposition of the liquor containing chlorides of sodium and calcium out of the ordinary ammonia process. Pearl hardening would be precipitated, and a solution of pure chloride of sodium originated. This solution, as soon as properly concentrated by boiling, may be again treated in the ordinary way for the production of bicarbonate of soda and white alkali.

At any rate this proceeding it to be highly recommended, for it possesses the great advantage that all materials may be conserved or reproduced. There is no loss of material whatever but the trifling though inevitable one caused by the manufacturing itself.

Chlorine is obtained in the form of hydrochloric acid, except the small permanently circulating quantity. All the sodium is converted into soda, and the pearl hardening contains sulphuric acid as well as calcium. The production of hydrochloric acid through the proposed way of operating is very well worth mentioning, as the ordinary ammonia process does not admit that result.

The new proceeding can be adopted in all those places where there is a good market for pearl hardening, which I have no doubt will be the case everywhere in Western Europe. Pearl hardening is a well-esteemed stuff for a great many sorts of paper. It is furthermore very available for the painting of cardboard as shown above. The box-makers using cardboard painted by means of pearl hardening will save any expenses for labels, &c., as all printing matters may be lithographically printed directly

upon the painted cardboard, and, by the modern box-making machineries, cardboard thus prepared can easily be shaped to boxes of any sort and size that will be required.

As shown by the aforesaid facts, the manufacturing of soda according to the ammonia process, even on a small scale pays very well. The profitable realisation of the returns must be taken into consideration to be sure, but, even without that good chance, the making of soda turns out most advantageously, in particular for large concerns carrying on the same in an auxiliary way in order to produce the soda required for the main works.

Owing to the Soda Rings driving up the prices for the article, it is worth while to keep this point in view.

As far as I know, some important German makers—being large consumers of soda—are about to prepare their own ammoniated soda, in order to become independent of the fluctuations of the market.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 304).

For evaporations with hydrofluoric acid, as also for ignition and fusion, the author uses platinum spoons of 9–15 m.m. in diameter, and for igniting or melting small specimens platinum wires, as for blowpipe work. The greatest care must be taken in cleaning these spoons and wires. The spoons should be of the short-handled pattern, made in one piece, without rivetting.

Bunsen burners with a double gas supply, which give a small luminous flame if the regulating tap is closed, are very suitable for micro-chemical work if the luminous flame is small enough. It must not be higher than 10 m.m. It is difficult to make the flame of a spirit lamp small enough. Fatty oils answer the purpose well if a single thick thread of cotton is used as a wick.

The ordinary dropping tubes yield drops of about 0.05 c.c.; these are much too large for micro-chemical work. If the utmost nicety is required, drops of 1 m.grm. may be used, which spread out on the glass to discs of 2 m.m. in diameter. The limits for the sensitiveness of reactions, as laid down below, refer to such milligramme drops.

In order to manipulate such small quantities of liquid we use capillary tubes, obtained by drawing out thin bent tubes. They have the advantage, as compared with slender pipettes, that they can be expeditiously prepared, which enables us to dispense with tedious and uncertain cleansing. For distilled water a pipette may be recommended with a point so fine that, if applied for a moment to the port-object, it gives drops of 2–3 m.grms.

For manipulating the reagents, may be used platinum wires of 0.5 m.m. in thickness, melted into glass rods, or glass threads of the same thickness. The hooks of a finer platinum wire, formerly recommended, have the advantage, when they are thoroughly cleaned, that they always take up approximately the same quantities of liquids. Their defect is that a perfect cleaning is not as easy as with a straight stout wire, which can be made perfectly clean in a few seconds by wiping, rinsing, and ignition.

Reagents.

A catalogue of reagents may be found in the *Annales de l'Ecole Polyt. de Delft*, 1891. It may here suffice to remark that some of them, e.g., the salts of cesium and thallium, are not used in the ordinary course of analysis. The manner of their application is peculiar, since they are used in saturated solutions, or even as powders. The reason of this is that we must work with the smallest possible volumes of liquid. Reagents in powder have also the advantage that they come into action more slowly

* *Zeit. Anal. Chem.*

and simultaneously in all degrees of dilution. Most reagents are used in such small quantities that a stock for more than a year's service may be kept in specimen tubes of the smallest sort. Hydrofluoric acid and ammonium fluoride may be conveniently kept in similar tubes of ebonite, in the caoutchouc stoppers of which thin platinum wires may be conveniently fixed, coiled up at their free end into a loop or a spiral.

The selection of reagents, even if arranged for all contingencies, takes up little room.

Operations.

The evaporation of dilute solutions is generally effected on the object glass. If high concentration is necessary, the solution is let fall, drop by drop, upon the heated spot of the glass, by means of a small pipette. A current of dry air expedites evaporation and prevents boiling. When the last drop is about half evaporated the object slip is quickly cooled. The partial evaporation of single drops is often requisite, and occasions much trouble to beginners. A thin glass and a small flame are the most essential conditions. The object slip must almost touch the point of the flame, and the refrigeration must be effected as quickly as possible. By means of the following simple expedient it is possible to evaporate the smallest drops over a free flame without the danger of their entirely drying up. Upon an object slip, and near one end, there is laid a covering-glass; the drop to be heated is placed upon this, and heated as usual over a small flame. When the proper degree of evaporation has been reached, the covering-glass with the remainder of the drop is made to slide upon the cold half of the port-object. Evaporation by heating the port-object always invariably occasions the formation of irregular crystals on the edge of the drops, and this evil is the more perceptible the further the heating extends over the glass. Evaporation at the ordinary temperature (e.g., in an exsiccator) generally produces uniform crystallisation; the same is the case if the glass is cooled and the drop is heated by blowing warm air upon it from the nozzle of a blowpipe strongly heated.

For sublimations the specimen is placed near one of the corners of the port-object and covered, after it has been moderately heated, with a shorter slip with its corners bent downwards. For sublimation at a red-heat, and for subliming fluorides, we use small platinum spoons covered with platinum foil or covering-glass. The necessary cooling is effected in this case by the application of a drop of water. For filtration there are substituted, as far as possible, decantation and absorption with filter-paper. It often occurs that a drop of liquid must be separated from crystalline or powdery sediment without the necessity for complete clarification. This can generally be effected as follows:—A clear portion at the margin of the drop is drawn out into a streak of 1 c.m. in length, and its end is gradually widened to form a drop. The speed at which the liquid streams over depends on the inclination of the port-object and on the expansion of the thread of liquid. The rest of the liquid is drawn away through the connective channel by means of a platinum wire held in a slanting position, and intercepted with a small roll of filter-paper. The washing is effected in a similar manner, small rolls of filter-paper serving to suck up the rest of the washing water. If complete clarification is needed, or in case of light flocculent precipitates, such as basic iron or aluminium acetates, the liquid may be allowed to subside in a tube pipette of 2 m.m. internal diameter, the upper end being closed with a wax plug. The deposition may be hastened by the addition of washed barium sulphate during precipitation, and by centrifugal action. If the liquid is sufficiently clarified allow it to flow, drop by drop, upon burnt clay or compressed filter-paper. Here it forms little lumps which can be washed with a couple of drops of water, and scraped off with a slip of sheet platinum.

(To be continued).

THE PROGRESS OF CHEMICAL THEORY: ITS HELPS AND HINDRANCES.*

By Dr. PERSIFOR FRAZER, Prof. of Chemistry.

It is the ordinary reproach to science of the ignorant and disingenuous, that its conclusions at any given period are no more stable than the wildest speculations of the fanatic and dreamer.

We read continually in the papers some arrant nonsense said to have been pronounced by "one of the eminent scientists" of such-and-such a place and time, which the course of events has disproved; and the public is left to the conclusion that the gains of science are only air castles certain to dissolve when they become unpopular, and certain to lose popularity when the first pleasurable effect of the announcement has passed away. The following extract, from the *St. Louis Republic*, will furnish a case in point:—

"It has only been sixty years since a great mathematician demonstrated that a steamship could never cross the Atlantic because it would be impossible for her to carry enough fuel to last during the trip. Before he had hardly deduced his calculations a steamer from America glided into port."[†]

The name of the eminent scientist is not mentioned, and it is safe to conclude that if any man made such an observation he either would have failed of recognition by the class to which he is said to have belonged, or he was false to the fundamental principles of inductive science. It is not the province of inductive science to establish what is impossible, but what is in various degrees likely. Its premises are facts and its conclusions are probabilities; in many cases weak, but in others so strong that they produce the same effect upon the mind as certainties. Nor is it true that the gains of science are evanescent. Parallel with the accumulation of observations run the generalisations upon them. These generalisations are usually passed through the purgatory of hypothesis before they attain the bliss of theory, but no theory is old enough yet to have become more than a theory, though some have stood so many tests of their truth as to carry the conviction of axioms.

In looking over the histories of the sciences one finds the same general course of progress. At the outset in the halcyon days of the old Greeks, it is likely that some wise words will be found to have been spoken concerning them all; words that astound us with the apparent insight they show into problems which it would seem that the last twenty-five centuries were needed to give. But the centuries were not all equally productive. There came across the path of every systematic study of the laws of nature, first the cultured blight of the Aristotelian philosophy, which assuming to know everything, in fact largely contented itself with verbal jugglery, whereas accumulation of facts was the only road to knowledge; obliterating the forward steps that had been made, and substituting in their place the evolution of the universe and its laws from within. It was a philosophy where the distinction between words and things was obscured, and

* Introduction to the Chemical Lecture Course at the Franklin Institute, November 10, 1890.

† In reference to the supposed steam engine prediction, Mr. W. P. Tatham calls my attention to the fact that the actual observation misquoted by the *New York Herald* for sensational or other satisfactory journalistic reasons, and repeated ever since (in spite of countless corrections), after the manner of the average erroneous newspaper paragraphs, was made by Dr. Dionysius Lardner and referred to the steamer of that epoch, which, according to his calculation, could only carry coals for a journey of 2000 miles, with due allowance for accident and delay. That he never entertained such an opinion as that above referred to is evident from the following language: "We are even now upon the brink of such improvements as will probably so extend the powers of the steam engine as to render it available as the means of connecting the most distant parts of the earth."

"The Steam Engine Familiarly Explained and Illustrated, &c.," by the Rev. Dionysius Lardner, LL.D., F.R.S., pp. 241–242, &c., &c. E. L. Carey and A. Hart, Philadelphia, 1841.

a natural fact was attained by means of a pretty syllogism.*

Vastly worse were the centuries which followed, known as the middle ages. Centuries of ignorance, selfishness, and crime; when the possession of any knowledge but that of an armourer was looked upon with distrust and ascribed to the devil.

The different natural sciences emerged from this barbaric condition one to three centuries ago, and under the liberty of enlightenment, with the stimulus of more general education, have attained an abode in the life of the race from which it is difficult to see how they can be displaced without such a general cataclysm as would nearly destroy the human race itself.

Amongst these sciences, that of chemistry has had such a marvellous career that it is, perhaps, the best example which could be selected of the progress just alluded to. It illustrates aptly not only the methods employed in building up an inductive science, but the things that have helped and those that have hindered a development which, nevertheless, in spite of all hindrances, must fill us with a sense of wonder.

Our reason for this is that from various causes the real growth of chemistry only began in the seventeenth century, and that even then it lost nearly a hundred years in the quagmires of a false hypothesis which not only directed the efforts of chemists into unfruitful fields, but destroyed the value of the conclusions they reached from their work. Yet, even with all these drawbacks, no domain of human investigation has been widened so rapidly and with such advantage to the world.

At the very outset of the subject we find a generalisation of old Democritus (who lived 450 B.C.) so astounding in its character and so accurate in most of its statements that only in the past few years have chemists been able to reach these profound thoughts thrown across the ages into the midst of the civilisation of our time, as the legend has it that Bruce's heart was thrown by the Douglas into the bosom of the Saracens to stimulate the ardour of the Christian Knights to charge and recover it. But, unfortunately, no such effect was produced by the good old laughing philosopher; though at a snail's pace, and after a lapse of 2300 years, we have reached the spot. Briefly, as transmitted to Epicurus, and expanded by Lucretius B.C. 99-55, it was this.†

The universe consists of atoms and space. The atoms are of many forms and of different weights, and the number of atoms of each form infinite. Change is only the combination and separation of atoms! Atoms are in constant motion. "First beginnings" or atoms are never destroyed or worn out. The difference between a hard body like iron, and a soft body like air, is that in the first the atoms move to and fro within small distances; in the soft body they move freely or rebound from each other only at long intervals.

Bodies are partly "first beginnings," partly unions of "first beginnings." The properties of the bodies formed of the groupings of "first beginnings" need not be like the properties of the "first beginnings" themselves. "It matters much with what others and in what positions the first beginnings of things are held in union and what motions they do mutually impart and receive."

These views are extraordinary, and, with the exception of the difference in the form of atoms, which is a point beyond what we have been able to reach even now, the above contains a very fair statement of the atomic theory which is held by the most advanced chemists to-day.

How Democritus could have reached such conclusions is a mystery, but his announcement of these recondite truths very well illustrates the fact that an hypothesis, be it never so beautiful and even true, if unaccompanied by

facts to support it in no way helps the progress of natural science. Like every other guess it indicates merely the frame of mind of the man making it. It is like a floating shadow on the sea of time. Perhaps it defines substance, perhaps only a cloud of fancy.

This seed thrown off by Democritus found no soil of facts on which to grow, from his time until late in the present century, although Gassendi, Canon, and Provost at Digue, in France, after ages of ignorance, proposed it again, but without proof; and it is thought to have influenced the minds of Newton and Boyle.

This then is one example of an occurrence in the history of the science which to all appearance neither helped nor obstructed its progress unless in the indirect way of teaching men's minds to grasp large and comprehensive thoughts. All could not have been ignorance and degradation in Abdera (Thrace), or Miletus, or Athens, where a language existed capable of conveying from mind to mind thoughts like these, and where a mind was capable of conceiving such thoughts.

It teaches the student of natural history a lesson in addition to that of the old traveller's speculations, and it may serve to illustrate the difference which the late Prof. Clifford of Cambridge pointed out between accepting those conclusions of natural science which one has been taught, but has not personally investigated, and accepting what is said to have been revealed, but which, it is acknowledged, is not susceptible of any proof. In the one case the way is open to any one to pursue any single direction which has been before taken; measuring and judging of the correctness of the steps of one's predecessor; but in the other case there is no path anywhere, and the correctness of the position assumed cannot be judged. It is the difference between, on the one hand, handing the keys of a hundred trunks to a custom house inspector, who has at best time to examine but one or two, asking him to satisfy himself of the accuracy of your description; and, on the other, telling him that something indescribable ought to convince him more thoroughly of the contents of the trunks which he cannot inspect than of those which he can. Speaking generally it may be said that a proposition of which the steps which led to its acceptance cannot be indicated and followed has no place at all in the domain of science, though it may be true.

Such propositions were those of Democritus above given, and it is quite just that in the absence of logical proof they should have been excluded from the realm of science, and that to him who first showed reason for believing them should be accorded the honour of their discovery.

Of much less importance is the next hypothesis of the nature of things which we find announced by Aristotle in his quadrilateral of states: solid, fluid, dry (or warm), and moist (or cold), or what he supposed to be the elements of all bodies, viz., earth, air, fire, and water. It was unfortunate, and yet in accordance with the usual march of events, that this utterly inadequate and narrow guess should have fettered men's minds for 2000 years, owing to the mighty hold which Aristotle took of all nations. (See Aristotle, "A Chapter from the History of Science," Lewes).

As his historian remarks, Aristotle's works had a prodigious influence in Asia, and Europe, and Africa; among the Persians, Arabs, and in Germany, where part of his ethics were read in the churches on Sundays instead of the Bible. In the middle ages, too, these elements of Aristotle were imbued with a mysticism more than Platonic.

It was the spirit of that middle age, when the ignorant classes being the powers, made patient scientific work difficult and dangerous, that learning was concealed under the mask of paradox and cryptogram as if it were a crime. Whatever Aristotle's view of his elements may have been, it took a new direction, beginning with Geber in the eighth century.

The first chemists were alchemists who sought the

* It is intended to refer here to the exposition of the Aristotelian philosophy by its disciples from about the time of the Christian era to the eighteenth century, and not to disparage the marvellous genius of Aristotle.

† Democriti Aderita operum fragmenta.

transmutation of base metals into gold; the philosopher's stone, and the elixir of life. These were represented by Geber (an Arabian alchemist of 760), Albert von Ballstädt (1193—1280), Roger Bacon (1214—1294), Raymond Lull (1235—1315), Arnald de Villanova, Caletonia (1235—1314), &c. Those who examined physical problems retained the Aristotelian view, while the alchemists took more or less modified forms of Geber's doctrine, that the metals were composed of mercury and sulphur. As an instance of the confusion which reigned in the ideas of this time, some believed that these constituents of metals were real sulphur and real mercury, while others believed that qualities were intended by these terms. Geber ascribed to the sulphur the property of giving different colours to the metals.

At the end of the fifteenth century the alchemists had added salt to mercury and sulphur. Many regarded the Aristotelian elements as the ultimate; and mercury, sulphur, and salt as the intermediate or proximate elements, as, for example, Basil Valentine, who extended the number of substances of which these were the ultimate elements, from metals to all known matter, but denied that they were the common substances which we know under their names.

In the early part of the sixteenth century the failure to find the philosopher's stone led to the decadence of alchemical or transmutation chemistry, and the rise of iatrochemistry or that of healing. Paracelsus (1493—1541) taught that in a burning body the sulphur quality represented the inflammability, the mercury the sublimation, and the salt the ashes.

From this to the end of the seventeenth century disputes as to tenets were numerous, but no real progress was made, Agricola (1490—1555) attacked Paracelsus and fell back upon Aristotle. Libavius wrote the first treatise on chemistry (1595). Van Helmont (1577—1644) denied all Paracelsus' views and sought an universal solvent, which should be a panacea. He first recognised the existence of gases and quantitative relations, and opposed Aristotle's doctrines that fire was a body or earth an element; but believed water and air were such.

Glauber (1603—1668), though possessing variable views, invented better means for separating bodies. Sumert (1572—1637), Willis (1621—1675), Lemery (1645—1715) believed in five first principles—mercury (spirit), sulphur (oil), salt, water (phlegma), and earth. Lemery taught that these were in rapid motion, and thus gave rise to the obvious properties of things. He explained the well-known phenomenon of the calxes of the metals weighing more than the metals themselves, by supposing that in burning they absorbed fire materials.

The real philosophy of chemistry commences with Robert Boyle (1622—1691), who denied the accuracy of the doctrines both of Aristotle, and the later alchemical and iatro-improvements upon them. He believed that heat had not the power to transform complex substances into their constituents, but, on the contrary, sometimes produced complex out of simple substances, and sometimes was without effect. Other agencies than heat could produce the same effects. He strongly denied that one could predict the number of simple substances as Aristotle and his successors had done. He thought it probable, however, that the so-called elements consisted of the same kind of matter, differing only in the size, form, &c., of their respective smallest parts (see Kopp's *Geschichte der Chemie*).

It is well to pause for a moment here to consider these logical and scientific views of Boyle, not alone because they introduced for the first time a rational inductive system of chemistry, emanated from the mysticism and superstition of the ancients, but also because they are typical of one of the greatest of helps to the progress of chemical theory, independent and fearless criticism.

Except the brilliant guess that the so-called elements consisted of the same kind of matter, Boyle's mission seems to have been to hew down the weeds and under-

growth which had impeded the march of the science; yet his services were invaluable, as without them no further progress could have been made. This fact illustrates also the injustice of the cry so popular in some cases when the fallacy of a proposition has been exposed:—

"What have you to set up in its place?"

Surely it cannot be required of him who discovers a flaw in a supposed explanation that he should be always ready with a sound explanation. The two characters of mind which are required to accomplish these very different tasks are entirely unlike.

Plato and Aristotle probably regarded the lightning stroke as a natural phenomenon, and could have refuted the popular belief that it was the missile from Zeus's hand, but it required dozens of centuries of observation before even the most remote approach to an explanation of the phenomenon could be given.

As soon as the ground is cleared of rubbish, other and more rational theories have a chance to grow. Therefore the iconoclast, if impelled by his sense of truth, and if considerate in his methods, is a necessary pioneer and axeman ahead of the great army of Science. It is so much easier, however, to throw down than to build up, that the iconoclast business is often overdone by those who are incapable of any more skilled service to Science, and who confound the art of attacking everything with the duty of overthrowing evil. All honour to Robert Boyle for calling a halt in the unbridled fancy of the chemists of his day, and clearing the way for a new era! All honour to his deep insight into the workings of Nature, that he announced independently what old Democritus had dimly foreshadowed 2000 years before; and what it was reserved for a great chemist now living to put in words and carry almost to the state of an accepted theory: yet to neither of them will belong the credit of demonstrating the unity of matter, but to some one, it would seem, who shall pass the speculative stage and offer proof. It looks as if this were not to be long delayed.

Both by Boyle's destructions and by his conceptions he aided the progress of chemical theory, as few have done since his time; and chemistry, or the study of the most intimate relations of matter, as distinguished from alchemy, magic, or the healing art, may fairly be said to have started with Robert Boyle.

Singularly enough the first sapling to spring up and occupy the new clearing made by Boyle was an error so gross that it seems to the youngest student of to-day grotesque in its clumsiness, and yet, defended by some of the subtlest of sophists, it took 100 years to overthrow it. And the most instructive part of its history is that it was finally overthrown by an argument which Boyle himself had employed,—which had been employed by other sceptics, and explained away by the phlogistonists, and was ultimately and successfully refuted with the same experimental proof by a countryman of Boyle. It is often the case that an attack in front, over the very ground of numberless previous repulses, is successful, and it was the case here, as shall be briefly shown.

Stahl (1660—1734) was a physician of independent views, who adopted Becher's theory of combustion or the changeability of bodies by heat. He believed that he had settled experimentally this question:—"Is a common quality present in sulphur and carbon? or is one contained in the other?"

The generally accepted view at that time was diametrically opposite to that which Boyle held of combustion, and might be stated thus:—Sulphur consists of oil of vitriol and some combustible body, which latter escapes in burning. Stahl combined oil of vitriol with an alkali, and, heating the combination with carbon, obtained an alkaline sulphide similar to that produced by sulphur and an alkali. From this, sulphur (or vitriol) can be separated.

Therefore, the combustible in carbon and sulphur was the same!

Heating calxes of the metals with carbon, there resulted the metals. The metals were then composed of the calxes and this substance. Fats and oils produced the same effect with the calxes, and, hence, in them too was the same combustible substance.

Stahl called this combustible "Phlogiston."

This hypothesis was rapidly installed into the rights and dignity of a theory, and rallied around it, as such, some of the brightest and best minds for three generations.

It was not only faulty in its conclusions, but inadmissible in its steps, and should have incurred the opposition of every intelligent man who understood the limitations of inductive philosophy; but it occupied the vacant space left bare by the labours of Boyle, and, with a growth as luxurious as it was pernicious to the attainment of truth, obstructed in many ways all valuable advance of chemical theory while it lasted.

It may not be amiss, before sketching its rise and overthrow, to point out here wherein its inherent fallacies should have condemned this hypothesis from the outset.

Hypothesis means a guess—a temporary structure erected by the employment of the imagination strictly governed by experience, for the purpose of more rapidly reaching a generalisation than by waiting for all the facts which in the end will be necessary to sustain a full-fledged theory. After one or two facts bearing on a subject are ascertained, it often happens that the mind is directed towards the possible existence of a law which would explain them both; but numerous unknown and untried experiments must result in a certain way in order that this supposed explanation may stand.

With time and a constantly increasing experience more and more such facts are ascertained. If all fall into their places the hypothesis grows stronger and stronger in probability, until, by a large accumulation of such corroborations, the hypothesis passes the undefined line which separates it from theory, and becomes a theory.

This theory then goes on increasing in strength by each additional fact which is found conformable to it, until its convincing force is almost as great to the mind as one of the facts which are the bricks of its construction.

But if, during this period of probation of an hypothesis or of a theory, a single fact is well authenticated which is inconsistent with it, the hypothesis or theory must be abandoned. Of course, in the case of a theory which had been tried and proven hundreds of times, and found to apply to newly-discovered facts, its abandonment would be held in abeyance until every effort had been made to prove the authenticity of the fact and its inconsistency with the supposed explanation; but if these were unalterably confirmed the hypothesis of theory must fall.

This constitutes the true principle of inductive philosophy, and only by pursuing this path rigorously can its processes lead to any good result.

(To be continued).

COTTON-BLEACHING WITH OXYGENATED WATER.

By M. PRUD'HOMME.

THE addition of calcined magnesia to oxygenated water has been recommended for bleaching cotton, but the superiority of the results obtained has not received any explanation. It depends, as I am about to show, on the formation of magnesium peroxide, which at 100° is more stable than hydrogen peroxide.

1. Oxygenated water at 6 volumes, diluted with 10 parts of water, was boiled for half an hour; its standard fell from 1000 to 100.

2. A similar quantity, with the addition of calcined

magnesia (5 per cent on the weight of the hydrogen peroxide), falls in strength only to 900.

3. Calcined magnesia is placed in contact with oxygenated water at 3 volumes, at the ordinary temperature. The duration of the contact varies from some hours to many days. It is filtered, washed on the filter, and the product dried at from 100° to 105°.

The determination of the active oxygen by means of a normal solution of potassium permanganate corresponds to the formula $3\text{Mg}(\text{OH})_2 + \text{MgO}(\text{OH})_2$. This body, by an alkaline reaction, loses all its active oxygen at about 300°.

Magnesium peroxide is also formed on dissolving the metal in oxygenated water. Weltzein considers the product of the reaction a soluble magnesium hydrate. It is easy to show that when evaporated to dryness it gives, with the ordinary tests, the well-known reactions of oxygenated water.

The oxides of zinc and cadmium (metals belonging to the same series as magnesium in Mendeleeff's classification) also give rise to peroxides.

The mixture of zinc oxide and peroxide corresponds approximately to the formula $2\text{ZnO} + \text{ZnO}(\text{OH})_2$.

Cotton bleaching with oxygenated water would remain unintelligible if we confined ourselves to consider it as a simple decolourising agent. It has a direct action upon the different bodies which bleaching has to modify or to eliminate, and even upon cellulose.

Action upon Fatty Bodies.

The saponification of the oils or fats is effected in part by the magnesia, but it is also due to the direct action of the oxygenated water. During ebullition there takes place an abundant liberation of carbonic acid; it may be derived from the oxidation of the glycerin, as it is verified directly. But the oxygenated water, very faintly acid, attacks also the neutral fatty bodies at ebullition, with the liberation of carbonic acid and a formation of fatty acids. These again are transformed by the mixture of oxygenated water and of calcined magnesia, and always with the production of carbonic acid. This happens with the stearic and the oleic acids of commerce. There must occur a partial transformation of this latter body into palmitic acid (as if by the action of potassa lye), for the product of the reaction, if suitably treated with an acid, is richer in soluble fatty acids than the oleic acid of which it forms a part.

The fatty bodies which remain upon the fibre in the state of magnesium oleates, palmitates, &c., are eliminated by a passage in weak acid, followed by an alkaline lye.

Action upon Cellulose.

In bleaching with oxygenated water the cellulose tends to become converted into oxycellulose. This is easily recognised by dyeing in basic colouring matters which fix themselves without a mordant upon oxycellulose.

The modification of the cellulose is more strongly marked if it has been mercerised, i.e., saturated with concentrated caustic soda before treatment with oxygenated water. The disaggregation becomes complete, and the tissue becomes a pulp if we add caustic soda to the bath of oxygenated water until it marks 6 to 8° I'w.

The action of oxygenated water upon cellulose is much increased by the presence of certain bodies, such as metallic oxides, which serve merely as a vehicle or intermediate agent for active oxygen. A swatch of cloth mordanted with iron, chrome, or alumina, and boiled with oxygenated water or magnesia for one to two hours, is profoundly attacked at the parts covered by the mordants. It is well, therefore, to let a treatment with weak acid precede the bleaching with oxygenated water, to eliminate the salts or the metallic tissues from the tissue.

The action of oxygenated water and that of cuprammonium upon cellulose present great analogies.

It is easy to show that the ammoniacal solution of copper oxide is an oxidising agent, by allowing it to act upon a

swatch dyed blue with indigo. The solution, if sufficiently diluted to produce no sensible alteration of the tissue, decolourised the blue in 24 hours in the cold, and in a few minutes at 60°. If the cuprammonium solution is sufficiently concentrated to weaken the fibre, this, if well washed and treated with a dilute acid to dissolve out the copper oxide, takes up a full shade on methylene blue: there is therefore a formation of oxycellulose.

A swatch of cotton cloth mercerised in caustic soda at 36°, and thoroughly washed, is left in contact for some hours with a cuprammonium solution of medium concentration. The fibre is more attacked than that of a check swatch which has not been mercerised.

We conclude from these experiments that, contrary to the received opinion, cellulose is attacked and transformed by contact with the reagent of Schweitzer. — *Comptes Rendus* (cxii., p. 1374).

NOTICES OF BOOKS.

Researches on Cobalt. An Inaugural Dissertation submitted to the Philosophical Faculty of the University of Erlangen. By HUGO REMMLER. (Untersuchungen über Cobalt. Inaugural Dissertation zur Erlangung der Doctor Würde bei der Lohen Philosophischen Fakultät der Universität zu Erlangen). Berlin: Dobrin.

THE author points out the discrepancies in the determinations of the atomic weights of cobalt and nickel as obtained by chemists of recognised standing. He quotes a table from the work of Cl. Zimmermann, in which the results vary in case of cobalt to 2.09 per cent of the total, i. e., from 59.87 to 58.57. In order to ascertain the cause of discrepancies, the more unsatisfactory as both cobalt and nickel have been made the subject of repeated examinations, he attacked a large specimen of the purest cobalt to be procured by the process of fractionation. By digesting cobaltic hydroxide for about nine months in aqueous ammonia, he obtained twenty-five extractions, twenty-four of which, after purification, were purified, and their atomic weights were determined. The values obtained ranged from 59.531 to 58.299.

All the preparations had been purified in exactly the same manner. It is to be remarked that the atomic weights found did not increase or decrease progressively. This fact seems to point to the conclusion that cobaltic hydroxide is either a compound or a mixture of two hydroxides, each of which is unequally soluble in the liquids employed. The author's results, therefore, seem to agree with the result of Krüss and Schmidt, that cobalt purified by the ordinary methods contains two components of different atomic weights.

Catalogue of Standard Second-hand and New Books, English and Foreign, on Chemistry and the Allied Sciences, Technology, &c., Offered by WILLIAM F. CLAY, 2, Teviot Place, Edinburgh.

THIS catalogue will be, we feel sure, of great interest to our readers. It is especially rich in sets of Journals and Transactions which are becoming increasingly scarce and difficult to procure. Thus we find here quotations of the *Analyst*, complete, from the beginning to 1886; the *Annalen der Physik* (Gren and Gilbert's), from 1792 to 1824; the *Cavendish Society's Publications*, complete; the *Journal of the Chemical Society*, from 1863 to 1890; the *Journal für Praktische Chemie*, from the commencement to 1860; the *Berichte der Deutschen Chemischen Gesellschaft*, from 1883 to end of 1889; the *Chemiker Zeitung*, 1881 to 1888; the *Comptes Rendus*, vols. i. to c., and various other important series, to which the librarians of scientific societies, colleges, &c., should have their attention directed. We find also odd volumes, which may often be required for completing sets.

There are many choice works from the library of the late Prof. Carnelley. There is a complete set of the *Pharmaceutical Journal* and *Transactions* from the outset to 1889, a series very difficult to procure complete.

As an instance of the reasonable character of the prices we find that the *Encyclopédie Chimique*, edited by Frémy, a work only completed last year and published at £60, is now offered for £25!

CORRESPONDENCE.

THE RELATION BETWEEN THE CHEMICAL CONSTITUTION OF CERTAIN ORGANIC COMPOUNDS AND THEIR ACTION UPON THE ULTRA-VIOLET RAYS. (A CORRECTION.)

To the Editor of the *Chemical News*.

SIR,—In your last issue Prof. W. N. Hartley points out that Dr. Krüss, in his memoir entitled "Beziehungen Zwischen Zusammensetzung und Absorption-Spektrum organischer Verbindungen," which appeared three years ago in the *Zeitschrift für Physikalische Chemie*, has attributed to me conclusions drawn from an examination of the action of certain organic compounds on the ultra-violet rays, which in reality were drawn by Prof. Hartley himself, in a series of papers which are well known to every English worker. I much regret that this is the case, and I am anxious to do whatever lies in my power to correct the error into which Dr. Krüss has undoubtedly fallen. At the same time, however, I must take very decided exception to the inaccurate and misleading account which Prof. Hartley has given of the facts of the case, and especially to the suggestion that I am in any degree responsible for the confusion. As far as I am concerned the facts are as follows.

Eleven years ago, when I was Demonstrator of Chemistry at the Pharmaceutical Society, I carried into operation a plan by means of which my advanced students might be kept aware of the progress which was being made in the various branches of chemical science. The plan was carried out in connection with a Students' Association which is attached to the Pharmaceutical Society's School. Certain members were appointed to report, from time to time, on recent chemical work. I undertook to deal with Organic Chemistry, and in July, 1880, now exactly eleven years ago, I made a report on the work done by Miller, Soret, and more recently by Hartley and Huntington, in tracing the connection between the chemical constitution of organic compounds and their action on the ultra-violet rays. The substance of this report, which took the form of a lecture, subsequently appeared in the *Pharmaceutical Journal* of July 17th, 1880,—not, however, in the portion of that journal which is devoted to original communications, but in the later portion in smaller type, and as a part of the account of the proceedings at the last meeting of the Students' Association. No one who read this report could possibly be under any misapprehension as to its character. Although the lecture was designedly a popular one, yet in the substance of it which appeared in print it was made quite clear that the experimental work had been done, and the deductions from it had been drawn by Messrs. Hartley and Huntington, whose names were duly mentioned, as were also the references to their original memoirs, which had been consulted in preparing the report.

From what I have written it will, I think, be clear that neither in the substance of my lecture nor in the mode of publication of the abstract of it was there anything likely to give a false impression as to my connection with the subject. A large number of similar reports have since appeared in more or less detail in the *Pharmaceutical*

Journal to the manifest advantage of advanced students connected with the Society, but, so far as I am aware, the present case is the only one in which confusion has arisen.

The annoyance which Dr. Krüss's mistake has quite naturally caused Prof. Hartley has, I am afraid (even after the lapse of three years), led him to make certain unwarrantable assertions which I feel compelled to refute.

Prof. Hartley asserts that Dr. Krüss has been misled into assigning to me priority in respect of this research on account of my lecture having dealt with results which Prof. Hartley did not actually publish until some months after the appearance of the abstract of the lecture. Prof. Hartley states that "by this report being quoted and referred to as an original contribution I also was misled and put to the trouble of consulting it. I then found that it was published actually prior to my papers entitled "Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra," for although they had been verbally communicated to the Chemical Society as early as June, 1880, and in writing on December 2nd of the same year, they were of necessity not published in the *Journal* until March, 1881, while Prof. Dunstan's report on them appeared in January. He thus appears to be entitled to priority in respect of these matters." As a matter of fact the assertions and implications here made are absolutely without foundation.

In the preparation of my lecture I used no information which had been published by Prof. Hartley later than June, 1880. As appears from the footnotes in the abstract of my lecture, the original memoirs were carefully consulted and I did not "merely make use of abstracts of them." Lastly, I would point out that my lecture did not appear in January, 1881, as Prof. Hartley asserts, but in July, 1880, so that it could not possibly have dealt with facts which Prof. Hartley did not publish until the following year (1881).

I think I have now gone into sufficient detail to show how inaccurate the premisses are from which Prof. Hartley has concluded that I am responsible for my "report being quoted and referred to as an original communication."

Since reading Prof. Hartley's letter, I have been considerably puzzled to understand how it has happened that my lecture has been dragged out of its original obscurity and "referred to as an original communication." I cannot find that the lecture was abstracted in any scientific periodical, and it is not likely that Dr. Krüss would naturally refer to the reports of the meetings of the School of Pharmacy Student's Association, which appear in the *Pharmaceutical Journal*, for information on such a subject, unless, indeed, his attention were specially directed to them.

In considering the different means by which prominence might have been accorded to my lecture, it occurred to me to refer to the bibliography of spectrum analysis drawn up by a Committee of the British Association in 1881, and there (York Report, 1881, p. 415) I was surprised to find the abstract of my lecture "quoted and referred to as an original communication," and my astonishment was considerably increased when I observed that Prof. Hartley was a member of the Committee which compiled this list of papers.

It is now clear upon whom rests the responsibility for Dr. Krüss's mistake. As, however, I am anxious that the confusion which Prof. Hartley assisted in initiating should as far as possible be obviated, it is my intention to address to Prof. Ostwald—the editor of the *Zeitschrift für Physikalische Chemie*—for insertion in his journal, a note, pointing out that my communication, to which Dr. Krüss has referred, is not an original contribution, but merely the substance of a lecture on recent advances in this department of physical chemistry; and that the conclusions he has attributed to me were drawn

by Profs. Hartley and Huntington, and published by them some time previous to the delivery of my lecture.—I am, &c.,

WYNDHAM R. DUNSTAN.

Research Laboratory,
Pharmaceutical Society of Great Britain,
London, June 29, 1891.

MISLEADING TITLES.

To the Editor of the *Chemical News*.

SIR,—The subjoined letter appeared in *The Standard* of Friday, June 26th, 1891.

If the Royal Society can do this, why cannot the Chemical Society?—I am, &c.,

PUZZLED.

SIR,—The attention of the President and Council of the Royal Society has been called to an advertising pamphlet, the title-page of which states that it is by Professor Harley Parker, F.R.S.

As the letters F.R.S. are used to denote that the bearer of them is a Fellow of the Royal Society, and as there is not, and never has been, a Fellow of the name of Harley Parker, I have been directed to request you to call public attention in your paper to this misuse of the initials F.R.S. The public will be able to judge of the intention with which they have been wrongfully assumed.

—I am, Sir, your obedient servant,

HERBERT RIX, Assistant Secretary to the
Royal Society.

The Royal Society, Burlington House, June 25.

ESTIMATION OF TANNIN.

SIR,—I should feel much obliged if you could give enclosed circular the publicity of your columns, as there may be many chemists who are interested in the matter whose names I do not know.—I am, &c.,

H. R. PROCTER.

Leather Industries' Department,
The Yorkshire College, Leeds, June 25, 1891.

In view of the serious discrepancies which often occur in the percentages of tannin found in gambier by different chemists, I have been requested by the Leeds Leather Trade Association to act in conjunction with Mr. R. G. Salomon, of Newark, N.J., Chairman of a Committee of the National Morocco Manufacturers' Association of the United States, to collect information with a view to the adoption by the two associations of a uniform standard method for the analysis of gambier. There seems no doubt that there is a very strong consensus of opinion in favour of the indirect gravimetric method, in which equal portions of the infusion of the tanning material are evaporated, in the one case after careful filtration through paper only, and in the other after the complete removal of the tanning matter by treatment with purified hide-powder; and the tanning matter is calculated from the difference of weight of the dried residues. I shall be glad, however, to receive any suggestions you may be good enough to make, either as to the general method to be adopted, or the details of preparing the infusion and absorbing the tannin, which are matters of considerable importance.

I am sending this circular to a number of chemists who are interested in the question: and I propose, before reporting to the Associations, to embody the information I receive in a paper for the Society of Chemical Industry, so that the matter may be verbally discussed at the different sections, and the prevailing opinion fully ascertained, as it is very desirable that a uniform method should be unanimously adopted.

HENRY R. PROCTER.

June 23, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxii., No. 24, June 15, 1891.

On Ferro-carbonyl: A Volatile Compound of Iron and Carbon Monoxide, and on Nickelo-Carbonyl.—M. Berthelot.—Iron in a certain state combines directly, and in the cold, with carbon monoxide. The iron is obtained by reducing ferric oxide (precipitated, washed, and dried with care) in a slow current of hydrogen at the lowest temperature possible. The reaction of carbon monoxide with iron thus prepared takes place at about 45°. The product is a gas. The author has re-examined the nickelo-carbonyl discovered by Mond, Lang, and Quincke, which is a liquid, boiling at about 46°. It is not appreciably absorbed either by water, dilute acids, or alkalis, or acid cuprous chloride. Its true solvent is the essential oil of turpentine. Carbon monoxide has thus the property of uniting in the cold with nickel, iron, and doubtless with other metals taken in a suitable condition. It forms thus an order of special compounds, analogous to compound metallic radicles. These compounds are capable of oxidation and of other reactions, forming complex organic compounds. From another point of view a compound of iron with carbon monoxide doubtless plays a part in various reactions observed in metallurgy, such as the precipitation of carbon from carbon monoxide in contact with iron, observed by Gruner; the formation of gaseous bubbles in the midst of softened iron, observed by Cailletet, &c. Certain transfers of matter observed either in cementation-pots or in Siemens furnaces are also connected with the existence of ferruginous compounds of this nature.

Researches on the Application of the Measurement of the Rotatory Power to the Determination of the Combinations formed by the Aqueous Solutions of Mannite with the Acid Sodium and Ammonium Molybdates.—D. Gernez.—The author has previously demonstrated that the solutions of active tartaric and malic acids when brought in contact with the aqueous solutions of inactive bodies, such as the molybdates, phosphomolybdates, tungstates, &c., form compounds which exert upon polarised light an action which is a number of times greater than that of the active body which they contain. He has now found that other active bodies which have not a double function (acid and alcoholic) lend themselves to a similar study. His observations have been in the first place made with mannite.

On Quinethyline: A Base Homologous to Quinine.—MM. E. Grimaux and A. Arnaud.—They give the generic name quinines to compounds of the general formula $C_{19}H_{21}N_3OOR$, R being any group whatever. The first term of the series is quinomethyline, or ordinary quinine, and the second term is quinethyline, a substance which they describe in the present paper. Its composition is $C_{21}H_{26}N_3O_2$.

On the Ureides derived from Normal Acids.—M. C. Matignon.—The author has obtained formylurea and acetylurea. Their formation heats are respectively equal to 119.3 cal. and 129 cal.

Method of Formation of the Methylcamphocarboxates of Methyl and Ethyl. Preparation of Methylated Camphor.—J. Minguin.—Not adapted for useful abridgment.

Nitrosocyanacetic Ethers.—P. Th. Müller.—The author obtains these ethers by causing amyl nitrite to act upon the sodium-cyanacetic ethers.

Bleaching of Cotton with Oxygenated Water.—M. Prud'homme.—(See p. 9).

Moniteur Scientifique, Quasnovella.
Series 4, Vol. iv., Part 2, No. 586.

Synthesis in the Group of Sugars.—E. Fischer.—A portion of a memoir inserted in the *Berlin Berichte*, vol. xxiii., p. 2114.

Limited Reactions.—M. Prud'homme.—A purely mathematical paper, incapable of abridgment.

Action of Mineral Acids in Saccharification by Malt and the Fermentation of Starches.—Dr. J. Effront.—In this chapter of his memoir the author considers the influence of hydrofluoric acid and of fluorides in the fermentation of amylaceous matters. He states that whilst in ordinary fermentations the yield of alcohol was only 43 per kilo. of starch, by the use of fluorides it is raised to 61.9.

On Recent Colouring Matters.—F. Reverdin.—The author mentions the oxidations of orthophenylenediamine effected by O. Fischer and E. Hepp; the combination of α - β dinaphthylamine with diazobenzene, by P. Matthes; the azo-colours containing the quinone group, by Dr. F. Kehrman (*Chem. Zeit.*); the transformation of acetone-oxalic ether into symmetric oxytoluyllic acid, by L. Claisen (*Berichte*); and the synthesis of chrysene and the accompanying hydrocarbons, by Kraemer and Spilker (*Berichte*).

Alkaloids, Pharmaceutical Products, Essences, and Extracts.—Notices of the mixture of fufurol and methylfufurol known as fucosol (*Leibig's Annalen*); of the phenole of oil of sassafras, by C. Pomeranz (*Monatshefte der Chemie*); on orthine, a novel hydrazinic derivative proposed for use as a febrifuge (*Pharm. Central Halle*); the examination of phenacetine, by J. Luttke (*Pharm. Central Halle*); on aristol—an iodine compound of thymol used by Dr. Eichhoff in the treatment of skin diseases (*Pharm. Central Halle*); the composition of gum tragacanth, which according to Prof. Maisch (*Romieu's Journal*), is:—

Moisture	18.92
Soluble gum	35.94
Insoluble gum	43.39
Ash	2.27

100.00

starch being totally absent; on the essential oil of betel, by Dr. J. F. Bykman (*Berlin Berichte*); composition of the seed of *Calycanthus glaucus*, a rosaceous plant common in Georgia, and the *Cardinas*, very poisonous to cattle (*American Chem. Journal*); the solanidine of potato shoots, by Jorissen and Grosjean (*Acad. Royale de Belgique*); the formation of hydrogen peroxide at the expense of ether, by W. R. Dunstan and T. S. Dymond (*Journal of the Chem. Society*); quantitative separation of strychnine and brucine, by J. E. Gerock (noticed under *Zeit. Anal. Chemie*); determination of benzoic aldehyd in bitter-almond water, by C. Denner (*Pharm. Central Halle*).

Review of Photography.—This consists of a lengthy memoir on "orthochromatism" in photography, on toning Eastman's paper by means of platinum and magnesium chloride, the elimination of hyposulphite, the preparation of ferric oxalate, toning with aristotype paper, and on negative varnish.

The Manufacture of Potassium Ferrocyanide.—Mr. Readman.—From the *Journal of the Society of British Industry*.

Affinity of Heavy Metals for Sulphur.—(*Wissens. Wochenschrift*).—Insoluble sulphides are able to precipitate other metals from solution in the state of sulphides whilst becoming themselves soluble. Thus, copper sulphide with a solution of silver nitrate gives a precipitate of silver sulphide. Silver, therefore, has more affinity for sulphur than has copper. In 1837 Anthon drew up a table of the metals in the order of their decreasing affinity

for sulphur. Silver comes first, then follow copper, lead, cadmium, iron, nickel, cobalt, and manganese. E. Schürman has resumed and enlarged the researches of Anthon. He arranges the metals as follows:—Palladium, mercury, silver, copper, bismuth, cadmium, antimony, tin, lead, zinc, nickel, cobalt, iron, arsenic, thallium, manganese. The saline solution of a metal of this series may be decomposed (at least in great part) by the sulphide of any of the following metals, i.e., the metals following in the above list. The decomposition is so much the more complete as the metals are more remote from each other in the series. The metals at the head of the series are those which have the strongest affinity for sulphur. This affinity decreases insensibly until we arrive at manganese, which has very little. Manganese sulphide is decomposed by the saline solutions of all the foregoing metals.

Vulcanisation of Caoutchouc: A Special Study on the Use of Sulphur Chloride.—C. A. Fawcitt (*Dingler's Journal*).—The author proposes, instead of free sulphur or antimony sulphide, the use of which requires an elevated temperature, to employ sulphur chloride dissolved in carbon disulphide. The materials must be pure; the carbon disulphide must contain neither free sulphur nor fatty or tarry substances. The author has patented another process, in which the sulphur chloride is employed without solvent in the state of vapour.

MISCELLANEOUS.

Wanklyn's "Water Analysis."—The issue of the eighth edition of this book moves me to put on record a slight historical sketch which perhaps may interest some of the readers of the *CHEMICAL NEWS*. The book may be said to owe its origin to the late Mr. Brayley, who was librarian to the London Institution when the Laboratory of the Institution produced the ammonia process. I had published the ammonia process of water analysis in my evidence given before a Royal Commission sitting in the House of Lords, and also in a paper read to the Chemical Society in 1867, and yet Mr. Brayley assured me that that would count for nothing unless I would write a book on the subject. Mr. Brayley was wise in his day and generation, and he was a librarian. I submitted, and with great reluctance sat down to write the first edition of the water-book, which was published in the spring of the year 1868. The book, which, by the way, was brought out at my risk, yielded a slight profit, and in 1870 a second edition was required. That edition—the Chapman edition—was edited by the late Mr. Chapman, who perished in an explosion of nitrate of methyl in a German factory, about a year after the issue of the second edition. In 1874 the third edition was called for, and with the advantage of seven years' practical experience of the ammonia process I re-cast the book, which then assumed its present shape. The reception of the third edition was most flattering to its author. The book was authoritatively declared to be a text-book on the subject. Since that time I have scrupulously maintained the integrity of the text and the essential part of the book, the section entitled *Water Analysis for General Sanitary Purposes* has come down to the present year without any textual alteration, except extension due to the insertion of the moist combustion process and a little amplification of the classification of drinking waters, on page 68. It is, indeed, true that since 1874 the book has increased considerably in thickness; but that is mainly owing to the development of the non-essential portions. The eighth edition, just sent out by the publishers, is an absolute re-issue of the seventh edition, all except one-half of page 54, which contains certain explicit directions for the working of the moist combustion process.—J. A. WANKLYN.

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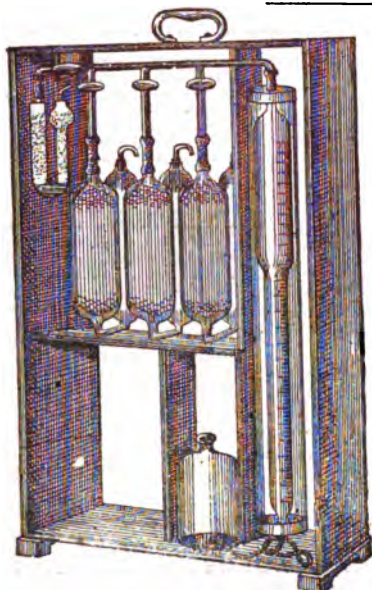
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THE CHEMICAL NEWS.

VOL. LXIV., No. 1650.

ON THE DETERMINATION OF THE AMOUNT OF FATTY MATTER PRESENT IN OLEINE (TURKEY-RED OIL).

By ROWLAND WILLIAMS, F.I.C., F.C.S.

DURING the last few years I have made a large number of analyses and experiments with the view of testing the accuracy of some of the methods which have been proposed from time to time for the estimation of the total fatty matter (fatty acids and glycerides), present in Turkey-red oil, or oleine, to use the name by which it is known commercially in this district.

It would answer no useful purpose, besides being extremely tedious, to describe every detail of the investigation referred to above, so I content myself with giving a brief summary of the main results obtained. For convenience sake the methods in general use may be divided into three groups:—1. Volumetric methods in which the volume of fatty matter resulting from the decomposition of a known quantity of oleine is ascertained and the percentage calculated therefrom. 2. Methods depending upon the use of some volatile immiscible solvent (such as ether or chloroform), for dissolving the fatty matter from a weighed portion of the sample, after decomposing with acid, and subsequent evaporation of the volatile solvent and weighing the fatty residue. 3. What is usually termed the "wax" method.

1. The volumetric method in some form or other is used by most manufacturers of oleine for the valuation thereof, and it is also in vogue in many dyeworks and printworks where the strictest accuracy is not required, as such a method is considered by many to be sufficiently exact for technical purposes. All the volumetric methods which I have met with for the determination of fatty matter in oleine are, however, distinctly wanting in scientific precision, for reasons which I shall explain presently. Originally, the volumetric method was carried out somewhat as follows, although various slight modifications have been introduced since by different operators:—A weighed quantity of the sample is placed in a graduated cylinder or other suitable apparatus, and, after decomposing with acid, with application of heat, the fatty matter is eventually read off and calculated to percentage. This is, of course, the process in its simplest form, and is obviously capable of considerable improvement. Whenever I have occasion to employ the volumetric method I use flasks of rather more than 5000 grains capacity, which I had made specially for the purpose. The necks of the flasks are moderately narrow, and are carefully graduated into 100 divisions, each representing five grains. I weigh some 400 or 500 grains of the sample (if that quantity be available), direct from a beaker into the graduated flasks, add a little dilute acid and some saturated salt solution and heat in a boiling water-bath for a short time, finally adding hot salt solution until the fatty matter rises to the graduated part of the neck. When cold, the fatty layer can be read off with a fair degree of accuracy, and is calculated *directly* to percentage. Several objections to this method will suggest themselves at once to anyone who has had much experience in the matter, but the gravest defect is, in my opinion, the confusion between weight and volume, which seems an inherent part of the process. As the specific gravity of the fatty layer varies in different samples of oleine, even when made entirely from genuine castor oil, it would obviously be difficult to make a correction; anyhow, to the best of my knowledge

this is never done. My experience of the volumetric method just described is that it almost invariably yields results from 2 to 4 per cent in excess of the truth, hence, I presume, the considerable degree of favour which it enjoys among manufacturers of oleine.

2. The ordinary way of applying this method consists of decomposing a weighed quantity of the sample with acid and then shaking with some volatile solvent (generally ether), in a separating funnel. The solution of the fatty matter is run into a weighed flask, the volatile solvent evaporated, and the fatty residue dried at the lowest temperature practicable. This method is theoretically an excellent one, but in practice I have found it somewhat unsatisfactory, owing to the fact that a certain amount of water and saline matter are always retained by the ether, rendering the drying of the fatty matter a difficult and tedious operation, besides necessitating a determination of the mineral matter in many cases. The following modification has been suggested by J. A. Wilson (*Journal of the Society of Chemical Industry*, vol. x., p. 28):—"10 c.c. of perfectly saturated salt solution are pipetted into a globular separator of about 100 c.c. capacity, and from five to six grms. of the sample poured directly into the separator. About 5 c.c. of HCl—*a* is then added and the whole thoroughly agitated, after which about 50 c.c. of ether is added and again agitated. The ethereal layer is received into a dry flask, and the aqueous layer again agitated with about 25 c.c. ether, which is received in the flask with the first extract. The ether is then evaporated and recovered, and the fatty matter in the flask dried by blowing dry air through about ten minutes. From 25 to 35 c.c. of really absolute alcohol is then added, agitated, and allowed to stand a short time, poured through a dry filter, the residue in flask washed two or three times by alcohol, and the filtrate and washings received in a tared flask, the alcohol evaporated, and the residue kept on the water-bath about one hour, whilst a current of purified air is continuously passed through the flask. The residue is then weighed and the percentage calculated." At first sight this method seems rather ingenious, but on putting it to the test upon several samples of oleine which have been sent to my laboratory for analysis lately, I found it to yield unsatisfactory results, invariably below the truth. I have arrived at this conclusion after making a considerable number of analyses and experiments, and my opinion is confirmed by the chemist in a well-known printworks in this district. The low results are, I believe, mainly due to decomposition of the fatty matter during the process of drying, but there are other possible sources of error. After the meeting at which the paper was read I called Mr. Wilson's attention to the danger of drying the fatty residue on the water-bath for so long a period as an hour, as decomposition would be certain to ensue to a greater or lesser extent. Mr. Wilson then informed me that he sometimes dried the fatty matter *in vacuo*, but as no mention is made of this in the published directions (which I have quoted verbatim), it would appear that he does not attach special importance to the point in question. Mr. Wilson seems to have made one very serious mistake in connection with this method. Like Mr. Guthrie, who published a new process for the estimation of fatty acids in alizarin oil last year (*CHEMICAL NEWS*, vol. lxi., p. 52), which I subsequently criticised and proved to be inaccurate (vol. lxi., page 76), Mr. Wilson seems to have made no effort to substantiate the accuracy of his method, but is apparently content to bring it forward mainly on account of certain novel features which it undoubtedly possesses. Before publishing a new process, or a modification of an old one, I consider it of the first importance that a chemist should employ every means in his power to verify its accuracy.

3. The "wax method," some form of which has been employed for a good many years, has now been adopted by nearly all the leading professional chemists as the most reliable for the determination of fatty matter in oleine. It has

been subjected at various times to a considerable amount of hostile criticism, and there is no doubt that in the hands of an inexperienced analyst the "wax method" is liable to give misleading results. On the other hand, when suitable precautions are taken by an expert in this branch of commercial analysis, I am convinced that no process can be more satisfactory. It is exceedingly simple—probably more so than any other gravimetric process we have for this purpose, and does not occupy an undue length of time in execution. The following is a description of the "wax method" as used in my laboratory:—Weigh 200 grains of the sample into a small porcelain basin, add 50 grains dilute hydrochloric acid (10 p.c.), and 300 grains saturated salt solution, then warm gently for a few minutes, add 200 grains white wax, and heat until the whole is perfectly liquid. Let cool, preferably for some hours, so as to allow the cake of wax and fatty matter to set as firmly as possible. Next, lift the wax, &c., out of the basin and wash the latter till all the salt is removed, and dry the basin thoroughly. Wash the cake of wax, &c., first with saturated salt solution, then with the smallest possible quantity of *very cold* water. It is advisable to pour the original fluid from the basin and also the washings into a clean beaker, in order to see whether any traces of fatty matter eventually rise to the surface. If not, it may be taken for granted that all the fatty matter from the 200 grains of the sample is adhering to the white wax. It is at this point that special care and experience are necessary, as the accuracy of the results depends almost entirely upon the manipulative skill with which the cake of fatty matter is now treated. The cake is dried as gently as possible (especially the under surface), by means of absorbent paper, and finally rendered perfectly dry either by leaving in a desiccator over sulphuric acid for some time, or by gentle heating accompanied by constant stirring. I have found the latter plan to answer equally as well as the former, provided that the temperature be not allowed to exceed 160° F. The basin and contents are allowed to cool and then weighed. On subtracting the weight of basin and wax from the total weight and dividing by two, the percentage of fatty matter is obtained. I have described the "wax method" with what may perhaps seem unnecessary detail, but this is not really the case. On the contrary, it is only by paying the strictest attention to all the little points which I have mentioned, together with constant practice in this class of analysis, that accurate results can be obtained. It is, indeed, probably inattention to detail and want of experience which has caused the "wax method" to be condemned as unreliable by certain chemists.

I have tested the "wax method" described above on three samples of oleine prepared by myself with extreme care from castor oil obtained from altogether distinct sources. The results obtained were very satisfactory, being, in fact, almost identical with theory in two out of the three samples. In the accompanying table will be found the figures yielded by a number of samples of oleine which I have examined during the last few months, by the methods referred to in the course of this paper. I think these will be sufficient to show the undoubted superiority of the "wax method."

Oleines.
Fatty Matter Per Cent.

Samples prepared by myself.	"Wax Method."	"Volumetric Method."	"Wilson's Method."
No. 1 (50 p.c.)	49'86	55'19	48'56
" 2 (61'36 p.c.)	61'58	64'28	58'87
" 3 (70 p.c.)	69'92	73'88	66'77
Samples received for analysis.			
No. 1	47'41	49'48	45'25
" 2	67'92	72'22	65'85
" 3	48'40	52'73	46'12
" 4	44'44	47'10	43'10
" 5	68'98	72'15	66'56
" 6	49'50	52'35	47'70

While not claiming special originality for the contents of this paper, I do claim to have proved that the "wax method," if carried out *exactly* as I have indicated, may be relied upon to yield more accurate results than any other which has been published hitherto for the determination of fatty matter in oleine. It is worthy of note that many dyers and calico-printers decline to accept results obtained otherwise than by the "wax method."

I cordially invite criticism from makers and users of oleine and from others interested in this important subject, and shall be glad to consider any suggestions or possible improvements in the methods which may be brought forward.

Laboratory and Assay Office,
25, Pall Mall, Manchester.
July 1, 1891.

THE FARADAY JUBILEE.

IN commemoration of the centenary of Faraday's birth, which occurs this year, two lectures have lately been given at the Royal Institution by Lord Rayleigh and Professor Dewar. We hope to publish these lectures in full before long. In the meantime we think it may interest our readers if we print a letter received from an old friend, long since dead, to whom the Editor wrote asking for his assistance in preparing an obituary notice for the CHEMICAL NEWS, on the occasion of Faraday's death. The following letter, received in reply, is as good a memorial of the illustrious dead as any that could be written at the present day:—

Cornwall, August 30, 1867.

DEAR CROOKES,—I should be proud indeed to be the spokesman of the chemical world in doing honour to Faraday's illustrious name on the occasion of his accession to immortality. But I should not dare to meddle with the laurels on so august a brow, without many days and nights of earnest research and meditation, to fit me for summing up, without omission, the splendid list of his imperishable labours.

Only in this reverential spirit of earnest solicitude to do aright, which is, if I mistake not, the philosophical counterpart of prayer—of the religious feeling—could so solemn a duty be fitly undertaken.

Only with the aid of other minds, kindred wth Faraday's in genius, and filled with the light of his manifold discoveries, could any one man's mind become an adequate mirror to reflect the gigantic Shadow that has just passed to its place in futurity.

For the present it is my fate to fulfil much humbler duties,—which, having undertaken, I have no right to set aside. For duty must still be done, even when such appeals as yours set the wings of the caged lark trembling, and point him upwards to his barred out home.

I must remain, therefore, a unit among the millions whose hearts do silent homage to the illustrious dead,—and can but watch, from afar, the starry coronation of which you invite me to be minister.

So best, perhaps. For, after all, the name and fame of Faraday transcend all pomp of celebration, all burning words of praise. For whose the pen to weave so bright a glory as that Electric fire which glows, through all the ages, round his brow, who first drew lightning from the lodestone as Franklin drew it from the sky?

In the moment of separation that little spark breaks forth—instantaneous, yet eternal. It is but one vivid point of the radiance that encircles his name, yet of itself it is glory enough.

From that spark a new branch of science has sprung; and under its creator's name, were it mine to carve his epitaph, these three should be the chosen words,

FULMEN ERIPUIT FERRO!

—Ever yours, faithfully,

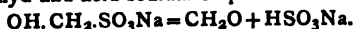
F. O. WARD.

THE FORMATION OF STARCH FROM FORMALDEHYD.

By TH. BOKORNY.

THE author assumes that formaldehyd is formed by the reduction of the carbonic acid on chlorophyll, and that carbohydrates (starch) are then produced by its condensation. Experiments made with pure formaldehyd to effect the formation of starch on the chlorophyll-organs of *Algae* miscarried on account of the poisonous action of this substance. Experiments with methylal, which easily splits up into methyl-alcohol and formaldehyd, were more successful as the formation of starch was ascertained. Still the results of these experiments were ambiguous, as the starch which was detected might have been formed from methyl alcohol.

Recently the author has experimented with sodium oxymethyl sulphate, which is readily broken up into formaldehyd and acid sodium sulphite:—



Carbohydrates are formed from the formaldehyd by condensation, $(\text{CH}_2\text{O})_6 = \text{C}_6\text{H}_{12}\text{O}_6$.

In order to prevent the injurious action of the primary sodium sulphite set free in the decomposition, di-potassium or disodium phosphate was added to the solution, which converted the acid sulphite into a neutral sulphite, with the simultaneous formation of a monophosphate.

The author placed *Algae* (*Spirogyra majuscula*) in a culture-solution containing 0.1 per cent of sodium oxymethyl-sulphonate and 0.1 per cent K_2HPO_4 , and allowed them to remain in air free from carbon dioxide with varying illumination. After five days enormous quantities of starch were found in the *Algae*. Even in six hours starch could be demonstrated in *Algae* which had been previously freed from starch.—*Deutsch. Gesell. Berichte und Chemiker Zeitung*.

THE PROGRESS OF CHEMICAL THEORY: ITS HELPS AND HINDRANCES.*

By Dr. PERSIFOR FRAZER, Prof. of Chemistry.

(Continued from p. 9).

THE obvious difficulty of the phlogistic theory was that the calx, which was considered the simple body, was heavier than the metal which was supposed to be the compound, and this circumstance was explained by supposing that the phlogiston which was absorbed from the fire when the calx was heated therein had the principle of "levity" as opposed to that of "gravity," and that the more of it which was collected in a body the lighter became that body.

Here was the unpardonable error of the phlogistonites in the defence of their theory.

Hofmann (1660—1742), the first to distinguish between magnesia and alumina, asked whether, instead of the above explanation of combustion, it was not the case that a metal received an "acid" when burned, which "acid" was re-absorbed when the metal was reduced. Besides him many others had noted the increase of weight on combustion, and Boerhave (1668—1738) had doubted the explanation above referred to.

The offence of which, as seekers after truth, the phlogistonites were guilty was that of calling into existence a substance which was diametrically different in its properties from any then known, and making this imaginary substance and its purely imaginary properties the basis of a theory.

Isaac Newton (1642—1727) had established, by his matchless investigations, commencing 1666, the nature and properties of matter, one of which, gravitation, was common to all bodies, and there was no excuse for an

hypothesis, after that date, which should deliberately rob matter of its one all-pervading attribute, unless some discovery had been made which seemed to support it.

If it be said that the observations on the combustion of bodies seemed themselves to furnish this proof, it must be admitted that for such an overthrow of all that had been patiently built up, some independent testimony unconnected with the then obscure phenomena of combustion ought to have been sought. This was an unpardonable deflection from the line of calm and dispassionate inquiry, and deserves to be held up for all time to the condemnation of scientific men as a warning, and its fate as an example,—the more so because as time went on, and the array of obstacles to the acceptance of this theory increased, its supporters were obliged to set up one after another distinct hypotheses to support the first untenable one, until the discussion partook more of the nature of those verbal juggles popular among the schoolmen of the Middle Ages than the efforts of students of Nature to arrive at a knowledge of her laws.

Marggraf (1709—1783) introduced into chemistry the study of reactions in the wet way, and thus laid the foundation of analytical chemistry. He recognised soda as an alkali, and magnesia and alumina as peculiar earths. Against the opinions of his predecessors he held that ammonia was not produced in the distillation of wood, &c., by the union of its constituents, but that it pre-existed in the wood.

J. Black, of Scotland, by his investigation of the alkalis, dealt the first serious blow to the phlogistic theory. He found that magnesia could be changed to "mild" from having been strongly alkaline, by exposure to air or by contact with "mild" alkalis. In other words, that it became carbonate of magnesia by exposure to the carbonic acid of the air or by treatment with the carbonates of the alkalis. Furthermore, he showed that what it lost or gained in these changes was a gas like air, which separated from it under treatment by acids with effervescence, whereas in its caustic condition acids dissolved it without effervescence. He also, with singular astuteness, established for his theory of combustion (which was to finally take the place of the phlogistic theory) the principle of latent heat. The immediate result of Black's discoveries was the rise of pneumatic chemistry or the chemistry of the gases.

Joseph Priestley (1733—1804) followed with more success than any other this line of investigation. He worked sporadically and without system, but with wonderful penetration discovered many things that had escaped the attention of better chemists. He himself called his achievements "sportsman's luck." He found the nitrogen left after combustion in air, and determined its proportion by volume. He regarded it as charged with phlogiston.

In 1774 he discovered oxygen in the oxide of mercury, and, recognising it as the supporter of combustion in the air, made it the measure of the destruction or devitalisation of the air. He discovered, besides oxygen and nitrogen, the reduction of the calxes by hydrogen. He also observed that by the passage of the electric spark through confined air in contact with moistened litmus, a new acid was produced which coloured the latter red. He furnished more material than any other chemist of the day for the destruction of the false phlogistic theory, but he was not only incapable of correctly reasoning on the facts which he had brought to light, but to the day of his death he maintained that his pivotal discovery, the corner-stone of the chemistry of to-day (as it was made by Lavoisier), was nothing but the production of dephlogisticated air.

It was a touching thought for those of us who, in 1874, assembled at his grave in Northumberland, Pa., to do honour to his memory as a great discoverer and a devoted friend of our young States when we threw off the English yoke, and to celebrate the centennial anniversary of the foundation of modern chemistry, in his isolation of

* Introduction to the Chemical Lecture Course at the Franklin Institute, November 20, 1890.

oxygen, that this great mind, so potent in the discovery in the science which he adorned, rejected the obvious fruits of that discovery, and insisted on rejecting the honour which should justly have been his.

H. Cavendish (1731—1810) was a more rigid investigator, who, having discovered hydrogen by the action of sulphuric or hydrochloric acid on iron or zinc, proceeded to examine exhaustively the properties of this new gas. He noted that like weights of metal gave him the same volumes, but that different weights of metals gave him different volumes of the gas. He concluded that hydrogen was either phlogiston or a combination of phlogiston with water, and that dephlogisticated air (oxygen) when combined with phlogiston (hydrogen) produces water.

He discovered the solubility of carbonates of the alkaline earths in excess of carbonic acid water, and discovered nitric acid. He was thoroughly saturated with the phlogistic theory, and all the useful deductions which his careful methods would have given him were thrown away by the distortions of the obvious bearing of his experiments which the phlogistic theory necessitated. When Lavoisier had triumphantly overthrown this dragon, Cavendish abandoned chemistry, simply remarking that it was hard to determine which of the rival theories was true.

Passing over the labours of the phlogistonists, Scheele, who discovered chlorine and fluo-silicic acid, and who believed light and heat to be fire and air; the first with more and the second with less phlogiston; and Bergmann, who systematised wet analysis, proved the existence of carbonic acid in the air, and introduced dry qualitative blowpipe analysis; we come to the first of a number of great figures in the history of modern chemical theory whose mission it was to open the door of the exact science of to-day and to indicate the route of those who followed him.

Lavoisier (1743—1794). His first chemical work was the experimental proof that water did not become an earth by boiling, but that the residue observed by boiling in a glass vessel was derived from the glass. His own discoveries are meagre in comparison with those of many of his contemporaries; but he greedily absorbed all that was discovered by others and changed it from crude and disconnected facts into an harmonious and consistent system.

All of his contributions to chemical science were of this character, even that great conception of the difference between the least distinguishable part of a certain kind of matter, and the least part which can take part in chemical reactions—the germ of the future distinction of the then unknown atom and molecule.

The last entrenchment of the phlogistonites was in the observed action of acids on certain metals whereby hydrogen (phlogiston) was produced. "If," they said, "a metal be not a combination of a calx with phlogiston, whence comes the phlogiston produced by the experiment?" The obvious answer was that it came from the acid, but what part? The acid was thought to unite with the metal and dephlogisticate it. Priestley and Cavendish had shown that hydrogen (phlogiston) and dephlogisticated air combined and in great part disappear. What became of them was not satisfactorily settled for a quite surprisingly long time. The fact that a little moisture was observed in the apparatus was probably ascribed to the sudden expansion and contraction of volume of the gases, since these matters and the hygroscopicity of the air were only beginning to be understood. When, therefore, Cavendish announced his discovery of the composition of water, Lavoisier applied it to the theory of combustion with such telling effect that it once and for all overthrew and destroyed phlogiston.

But though this was a glorious service of Lavoisier, it was far from all that chemistry owes to him. The new conceptions required a new language to express them, and Lavoisier with Guyton de Morveau established a system and a nomenclature so perfect as to form the framework enclosing within itself all systems which followed.

A series of definitions and rules for naming new combinations as well as a partial list of elements were parts of this system.

Lavoisier came back to Robert Boyle's definition of an element as a body which cannot be decomposed into simpler ones. The table of these elements, published by the French colleagues, contains also heat and light, but this was not in conformity with the opinion of Lavoisier, who was far too careful a student of nature to commit himself to any such gratuitous assumption; but rather more probably a concession made to the defeated phlogistonists and a means of avoiding the necessity of explaining that about which the views of scientific men were very conflicting, and nothing was certainly known.

One generalisation Lavoisier allowed himself, and that was that all acids contain oxygen (hence the name he gave to that element). It is curious how fate punishes such generalisations whenever they are made in the infancy of our knowledge on any subject. This generalisation reflects great credit upon its proposer, and shows a rapid and profound insight into many facts, but it was not many years afterwards pronounced, and is now generally considered, a fallacy, and yet if we interpret it to mean the exhibition of acid characters such as the reddening of litmus and the effect upon the senses, Lavoisier was not entirely wrong, since these characters are inseparable from the presence of water which contains oxygen.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

June 18th, 1891.

Prof. A. CRUM BROWN, F.R.S., President, in the Chair.

MR. F. J. BLOOMER was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. William P. R. Newlands, Rosa, North-West Province, India; Laurence Priestley, Forest View, Noel Street, Nottingham; Thomas Armistead Ward, Preston Road, Blackburn.

The following were elected Fellows of the Society:—Tom St. John Belbin; Edward Brown; Ernest A. Congdon, Ph.B.; W. Porter Dreaper; William Duncan; Alfred John Gregory; Frederick R. Holloman; John Knowles; Frank H. Leeds; Robert Andrew Scott Macfie; Arthur Michael; Thomas Mitchell; Harry Joseph Marston Mousley; James Lane Notter, M.D.; F. M. Perkin; Edward Rhodes; Edmund Charles Rossiter; John Shields; Frank O. Solomon; John Taylor; Frederick Tetley; Dr. Otto Carl Weber; Seward W. Williams.

The following papers were read:—

29. "A Note on Some Interactions of Dehydracetic Acid." By J. NORMAN COLLIE, Ph.D., F.R.S.E., University College, London.

During the last six months the author has been working with large quantities of dehydracetic acid, and he finds that several important reactions of this interesting substance have hitherto escaped notice.

In its preparation, by passing ethylic acetoacetate through a red-hot tube, it is stated that alcohol is formed; the author finds that large quantities of ethylene gas and acetone are produced as well. He also finds that dehydracetic acid is volatile to a considerable extent with steam, and is also decomposed by boiling with water to a small extent into carbon dioxide and dimethylpyrone—



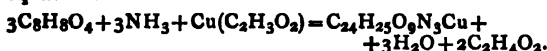
In the evaporation, therefore, of a solution of the acid,

a large quantity of the acid is lost. This decomposition into dimethylpyrone is effected far more readily if the acid is boiled with strong chlorhydric acid; if 50 grms. are boiled with the ordinary fuming acid, in about half an hour the whole is converted into carbon dioxide and a soluble compound of dimethylpyrone with hydrogen chloride. This hydrochloride crystallises from strong solutions in magnificent groups of tabular crystals. Feist states (*Annalen*, cclvii., 253) that chlorhydric acid is almost without action on dehydracetic acid.

The barium salt of dehydracetic acid seems to be not a salt of the compound $C_8H_8O_4$, but of the true tetracetic acid, $C_8H_{10}O_5$, and has the formula $(C_8H_9O_5)_2Ba$.

A curious copper salt has been obtained. If dehydracetic acid be added to a solution of copper acetate in a large excess of ammonia, on allowing to stand a pink insoluble salt separates. This salt is very stable, and is not decomposed even when boiled with sulphuretted hydrogen; but if chlorhydric acid is added it is at once decomposed and dehydracetic acid is re-formed.

The formula of the salt seems to be $C_{24}H_{45}O_9N_3Cu$. Such a salt could be produced according to the following equation:—



30. "The Lactone of Triacetic Acid." By J. NORMAN COLLIE, Ph.D., F.R.S.E., University College, London.

In a paper which the author communicated to this Society some short time ago (*Trans. Chem. Soc.*, 1890, 189) on the constitution of dehydracetic acid, he pointed out that if the formula which he proposed for dehydracetic acid were the correct one, it would then be the δ -lactone of tetracetic acid. The following list was then given, which was intended to show the connection between the condensed acids formed from acetic acid:—

$CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot COOH$, tetracetic acid.
 $CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot COOH$, triacetic acid.
 $CH_3 \cdot CO \cdot CH_2 \cdot COOH$, diacetic acid.
 $CH_3 \cdot COOH$, acetic acid.

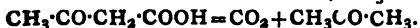
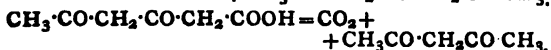
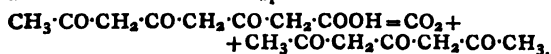
At that time no acid corresponding to triacetic acid was known. Since then the author has, however, been able to obtain the lactone of this acid by the action of 90 per cent sulphuric acid on dehydracetic acid at a temperature of 130–135° C.:—



It crystallises from water in fine needles, m. p. 183° to 189° (corr.).

The properties of this new lactone resemble those of dehydracetic acid. It does not form a stable ammonium salt, for, on evaporation of a solution of the acid in ammonia over sulphuric acid *in vacuo*, a certain quantity of the acid results.

When boiled with acids or water it yields carbon dioxide and acetyl acetone, resembling dehydracetic acid and diacetic acid in this respect:—



When warmed with strong solution of caustic soda, acetone and acetic acid are produced.

With bromine a mono-substituted bromine derivative is formed (m. p. 200–205°):—



If treated with hydroxylamine an hydroxime is formed, crystallising in long needles (m. p. 230–231° (corr.)).

And finally, if the ammonium salt is heated a nitrogen compound is produced, which is either a pyridine or pyrrol derivative, as it does not give any ammonia when heated with caustic soda:—



The investigation of this new compound is not yet completed.

31. "The Refractive Power of Certain Organic Compounds at Different Temperatures." By W. H. PERKIN, Ph.D., F.R.S.

Having found that the magnetic relations of substances, when examined at temperatures wide apart, showed that certain variations took place after allowing for change of density, experiments having been made by the authors in reference to the refractive power of liquids under similar circumstances. After describing the apparatus used, results are given showing that the specific refractive energy of the substances examined is not constant for all temperatures. The experiments were made at temperatures from about 14 to 92, and for the lines A, C, D, and F, the differences obtained were calculated for a variation of 100°, so that comparison could be more easily made, and are as follows:—

	$\frac{\mu_A - 1}{d}$	$\frac{\mu_A - 1}{d} \cdot p$
Aniline	0.00310	0.2897
Toluene	0.00329	0.2910
Heptane	0.00291	0.2914
Dimethylaniline ..	0.00253	0.3057
Phenyl iodide	0.00214	0.4378
Oily iodide	0.00190	0.4549
Cinnamic ether ..	0.00324	0.7080
Methylene iodide ..	0.00401	0.8685

By comparing the lines A and F it was also found that the dispersion was slightly diminished by rise of temperature. When calculated by Lorentz's formula, the numbers gave higher results for high temperatures than for lower ones, showing the formula is not suitable for the calculation of experiments made at high temperatures. Ketteler's experiments with water, alcohol, and carbon disulphide are also referred to. The influence of heat, therefore, affects both the refractive power as well as the magnetic rotatory power of substances; the results, however, are not comparable as to the extent of change.

DISCUSSION.

Dr. GLADSTONE remarked that in the original paper by Mr. Dale and himself, published in 1863, they had, as the result of an examination of twenty-three different liquids, come to the conclusion that—

$$\frac{\mu - 1}{d}$$

was "nearly a constant" at all temperatures. They had tested this for the theoretical limit of the spectrum according to Cauchy's formula, as well as for the lines A and H. Landolt and Wüllner seem to have expected that the slight differences recorded were due to experimental error, but on carefully repeating the experiments they arrived at a similar result. Dufet, in 1885, published an elaborate paper, in which he proved that the general law was not absolutely true, but a near approximation. Nasini and Bernheimer, in 1884, published very careful observations both on saturated and unsaturated compounds, dealing both with the specific refraction and dispersion; while Weegman and others have also contributed material to the general investigation of the subject.

Dr. Perkin's experiments were particularly valuable on account of the indications they give that the rate of change of specific refraction is greater at high than at low temperatures, and as they afforded clearer proof than has been hitherto given that the specific dispersion does increase with the temperature. If it should be found to be a general fact that the change is proportionally greater in saturated than in unsaturated compounds, and still greater in such bodies as cinnamic ether, another connection will have been established between this phenomenon and what we already know of refraction, dispersion, and magnetic rotation.

The observation that the values decrease as the temperature rises if calculated by the old formula, while they

increase as calculated from Lorentz's formula, seemed to be an argument in favour of the older formula; as the hotter liquid is approaching the condition of a gas, and it is well known that the refraction of a substance is somewhat smaller in the gaseous than in the liquid state.

Professor THORPE said that it would be specially important to study the influence of temperature on refractive power in the case of liquids, such as acetic acid, which were believed to undergo molecular change; and it would also be interesting to know what was the behaviour of the phosphorus compounds, as the optical properties of many of these were most anomalous.

Mr. HIBBERT thought that the superiority of the—

$$\frac{\mu - 1}{d}$$

formula over Lorentz's formula brought out by Dr. Perkin was an important result.

32. "*Notes on a Volatile Compound of Iron and Carbonic Oxide.*" By LUDWIG MOND, F.R.S., and F. QUINCKE, Ph.D.

The authors describe experiments from which they conclude that iron forms a volatile compound with carbonic oxide of the formula $\text{Fe}(\text{CO})_4$ corresponding to that of nickel. Very finely divided iron—obtained by reducing iron oxalate by hydrogen at a temperature but little exceeding 400° , and allowing it to cool to 80° in hydrogen—when heated in an atmosphere of carbonic oxide, gave a gas which burnt with a yellow flame; and on passing the gas through a heated tube, a mirror of iron was formed at between 200° and 350° , while at higher temperatures black flakes of iron and carbon were deposited. Only about 2 grms. of iron, however, was volatilised after six weeks' treatment of 12 grms. of the metal; it was necessary every five or six hours to interrupt the operation and to re-heat the iron to 400° in hydrogen during about twenty minutes. When passing carbonic oxide at the rate of about 2½ litres per hour, not more than 0.08 grm. of iron was volatilised, corresponding to less than 2 c.c. of the compound $\text{Fe}(\text{CO})_4$ in a litre of gas. The authors have effected an analysis of the compound by passing the mixture of gases into mineral oil boiling between 250° and 300° , and heating the solution so obtained to 180° ; iron free from carbon is then deposited, and carbonic oxide gas is evolved. Five analyses are quoted, the results of which give a ratio of Fe : CO, varying only from 1 : 4.03 to 1 : 4.264.

DISCUSSION.

Dr. ARMSTRONG said that the authors' discovery was even more interesting than that of the nickel compound which they had previously described in conjunction with Dr. Langer, on account of the explanation which it might be held to afford of the permeability of iron by carbonic oxide at high temperatures, as well as of the production of steel by the cementation process, phenomena to which Graham had drawn attention. Just as platinum was permeable by hydrogen and silver by oxygen at high temperatures, so iron was permeable by carbonic oxide: it might be supposed in each case, because a dissociable compound of the metal with the gas was formed.

Professor THORPE, after referring to the value of authors' observation as shedding light on the production of steel by the cementation process, stated that in studying, in conjunction with Mr. Ellis, the interaction of nitrogen peroxide and carbonic oxide under the influence of finely divided platinum, he had recently had occasion to observe that platinum had the property of causing the separation of carbon from carbonic oxide.

Mr. MOND, in reply, said that, although the application of their discovery in the directions indicated had not escaped their notice, they had refrained from discussing such matters, as the compound was only obtained at low temperatures.

Dr. ARMSTRONG said that this might well be the case; but, as Mr. Mond and Dr. Quincke had established the

all-important fact that iron had a specific affinity for carbonic oxide, the argument he had used would apply, although the compound might not be sufficiently stable at high temperatures to exist alone.

33. "*The Formation of Salts—a Contribution to the Theory of Electrolysis, and of the Nature of Chemical Change in the Case of non-Electrolytes.*" By HENRY E. ARMSTRONG.

The author draws attention to the recent researches of Claisen, W. Wislicenus, and others, which clearly show that ethereal salts, such as ethylic acetate, form compounds with sodium ethylate, and to the bearing which these results have on the theory of the formation of salts generally. It may be supposed that in all cases the acid and the "base" in the first instant combine, and that the salt is formed by subsequent interactions within the molecule. In like manner, acids form dissociable compounds with water, and it is by the occurrence of change within such systems under the influence of an electromotive force that electrolysis is effected.

In those cases in which the compound is highly unstable and prone to dissociate, the opportunity for change to take place within the system is but slight, and consequently the acid is a weak one, and its solution of relatively low conducting power. In the case of non-electrolytes the occurrence of change may, in like manner, be supposed to occur within complex systems formed by the union of the interacting substances—systems which are comparable with those formed by the union of acid and "base."

34. "*Dibenzyl Ketone.*" By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol. Dibenzyl ketone was prepared by Popow (*Ber.*, vi., 560), by the action of heat on calcium phenylacetate.

The author finds that when the calcium salt, dried at 130° , is heated in a hard glass tube in a combustion furnace, the yield is very poor, even when the temperature is kept as low as possible, and when a current of dry carbon dioxide is passed through the tube. After laborious purification of the product, not more than 27 per cent of the theoretical amount of pure ketone was obtained.

The action of heat on the calcium salt was then more carefully studied, and it was found that the decomposition begins at about 360° , and is very rapid at 445° , the boiling-point of sulphur.

A considerable quantity of calcium phenylacetate was then heated by means of the vapour of boiling sulphur in a special apparatus described fully in the paper. More than 50 per cent of the theoretical was obtained by crystallisation of the crude product from small quantities of ether, and by fractionation and subsequent re-crystallisations of the residues, the total yield of pure ketone was increased to 76.6 per cent.

Pure dibenzyl ketone melts at 33.0° , and boils at 330.55° under normal pressure.

35. "*The Vapour Pressures of Dibenzyl Ketone.*" By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol.

Constant temperatures above 280° , the boiling-point of bromonaphthalene, may be obtained by means of the vapour of mercury boiling under known pressure, but there are serious objections to this substance. Benzophenone gives very good results according to Crafts (*Amer. Jour. Sci.*, v., No. 5), but the boiling-point, 306° , is not sufficiently far removed from that of bromonaphthalene to give a good range of temperature. Dibenzyl ketone boils at 330.55° , and although it suffers a slight amount of decomposition on long continued boiling, the temperature of the vapour is not perceptibly effected. The ketone may also be readily purified by re-crystallisation from small quantities of ether.

The vapour pressures from 230° — 280° were determined in a modified distillation bulb, the temperature being measured with a mercuryl thermometer standardised by means of bromonaphthalene. At higher temperatures a

mercury vapour pressure thermometer was employed, and the ketone was boiled in a wide glass tube, enlarged into a bulb at its lower end.

Four series of determinations were made with very concordant results.

The logarithms of the pressure were mapped against the temperature, and the constants for Biot's formula ($\log p = a + \frac{b}{t}$), were calculated from the values at 230°, 280°, and 330°.

From these constants the vapour pressures were calculated at each 10° from 230—330°, and for each degree from 280—330°.

The results are tabulated in the paper.

36. "*The Vapour Pressures of Mercury.*" By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol.

In vol. xlix., p. 37—50, of the *Trans.*, an account was given by Dr. Ramsay and the author of determinations of the vapour pressures of mercury at several widely different temperatures, and tables of vapour pressure, based on these results, were added. The highest temperature at which observations were made was that of the vapour of sulphur boiling under atmospheric pressure, and in calculating the results the boiling-point of sulphur given by Regnault was taken as correct.

From a recent research by Callendar and Griffiths (*Phil. Trans.*, clxxxii., A, 119), it appears, however, that Regnault over estimated this temperature by nearly 4°, and the vapour pressures of mercury at high temperatures therefore require correction.

Messrs. Callendar and Griffiths have also re-determined the boiling-point of mercury by means of their platinum thermometer, and the temperature they have observed is about 1.5° lower than that given in the tables of Ramsay and Young.

Two additional observations of the vapour pressures of mercury at 183.75° and 236.9° have been made, and from the previous results by Ramsay and Young (corrected at the highest temperature for the alteration in the boiling-point of sulphur), the boiling-point of mercury given by Callendar and Griffiths, and the values at 183.75° and 236.9°, the vapour pressures of mercury at each 10° from 180—480°, and for each degree from 330—360° have been re-calculated, and the tabulated results, with an account of the method of calculation, are given in the paper.

Extraordinary General Meeting, June 25th, 1891.

Prof. CRUM-BROWN, President, in the Chair.

The request of certain Fellows to the President to summon an Extraordinary General Meeting of the Society and the notice convening the meeting were read, and on the motion of the PRESIDENT it was agreed that the proposals submitted for amending and altering the bye-laws should be taken as read, printed copies having been circulated among the Fellows.

The PRESIDENT suggested that the most convenient course would be for the Fellows at whose request the meeting had been called to explain and justify in general terms their proposals, and to leave the discussion of details to a later period. Mr. JAMES WILSON, however, urged that as specific resolutions had been submitted, the several bye-laws should be separately considered, and the President having agreed that this course would be in accordance with his ruling if the motion were confined in each case to an affirmation of the principle, Mr. WILSON moved:—"That Bye-law I. be altered in the sense indicated by the clauses already in the hands of the Fellows." He then indicated, with special reference to Clause 3, the reasons which, in the opinion of the memorialists, rendered such alterations desirable.

The motion was seconded by Dr. TEED.

Prof. TILDEN, in his capacity as President of the Institute of Chemistry, strongly deprecated the proposal that

Fellowship of the Chemical Society should be regarded as a professional qualification.

Mr. CARTEIGHE then moved the following amendment:

"That this meeting declines to pledge itself to any amendment or modification of the bye-laws which has not been approved and recommended to the Fellows for adoption by the Council."

Sir F. A. ABEL seconded the amendment.

Mr. CASSAL, Mr. LLOYD, and Dr. NEWTON addressed the meeting in support of the original motion. Mr. WARRINGTON, Mr. PAGE, Dr. ODLING, and Mr. FRISWELL spoke in favour of the amendment.

Mr. CLAYTON spoke in answer to objections made by Mr. Page to the use of the letters F.C.S., &c., under certain circumstances.

Mr. GOFFIN also spoke.

Mr. Lloyd and Dr. Teed having been nominated tellers for the original motion, and Messrs. Groves and Warrington for the amendment, the meeting then divided.

The votes recorded were—

For the amendment . . .	137
Against " . . .	47

Majority for the amendment . . 90

Prof. ODLING then took the Chair, and declared the following resolution carried:—

"That this meeting declines to pledge itself to any amendment or modification of the bye-laws which has not been approved and recommended to the Fellows for adoption by the Council."

On the proposal of Dr. TEED, seconded by Mr. CARTEIGHE, a vote of thanks to the President for his conduct in the Chair was carried.

PHYSICAL SOCIETY.

June 26th, 1891.

Prof. W. E. AYRTON, F.R.S., President, in the chair.

OWING to an examination being conducted in the Physical Laboratory of the Royal College of Science, the meeting was held in the Central Institution of the City and Guilds of London Institute.

Mr. J. ENRIGHT, B.Sc., was elected a member of the Society.

The following communications were made:—

"*The Construction of Non-inductive Resistances.*" By Prof. W. E. AYRTON, F.R.S., and Mr. T. MATHER.

In making some transformer tests, about three years ago, the authors had occasion to consider the construction of electric conductors the impedances of which should be practically equal to their resistances. This condition could only be fulfilled by making the inductance small in comparison with the resistance, and, as the former does not depend on the material employed (excepting iron), it was important to use substances of high specific resistance. Carbon or platinoid being available, the latter was chosen on account of its low temperature coefficient. One form of resistance exhibited consisted of strips of thin sheet platinoid, about 6 m. long and 4 c.m. wide. Each was bent at the middle and doubled back on itself, thin silk being placed between the contiguous parts and narrow ribbon used to bind the parts together. Twelve such strips arranged in series had a resistance of 2.95 ohms, and would carry a current of 15 amperes without changing its resistance more than one-tenth per cent. This strip resistance was made by Messrs. C. G. Lamb and E. W. Smith, who at that time (1888) were students in the Central Institution, and to whom the authors' best thanks are due for the praiseworthy manner in which they surmounted the difficulties which presented themselves. Another form of resistance, designed for

portability, consisted of bare-wire spirals, each length having a left-handed spiral placed within a right-handed one of slightly larger diameter, and the two being connected in parallel. This device was found to reduce the inductance to one-tenth or one-twentieth of that of a single spiral, according as the diameters of the spirals approach towards equality. When the spirals are made of platinoid wire the ratio of inductance to resistance is very small, averaging about 1-500,000th.

"On the Influence of Surface Loading on the Flexure of Beams." By Prof. C. A. CARUS-WILSON.

Referring to the practical treatment of problems on beam flexure as based on Bernoulli's hypothesis that the bending moment is proportional to the curvature, the author pointed out that this assumes that the cross sections remain plane after flexure, and neglects the surface loading effect. The present paper describes experiments made to determine the actual state of strain in a beam doubly supported and carrying a single load at the centre, the effect of surface loading being taken into account. The method of investigation assumes that—

(1) The true state of strain at the centre of a beam may be found by superposing on the state of strain due to bending only that due to surface loading without bending.

(2) The state of strain due to surface loading only may be found, with close approximation to truth, by resting the beam on a flat plane instead of on two supports.

(3) The strain due to bending alone may be obtained from the Bernoulli-Saint-Venant results.

Before proceeding to describe the experiments, a short account of the mathematical work previously done on the subject was given. The nearest approach to the particular case here dealt with had been worked out by Prof. Boussinesq, who has shown that, for an infinite elastic solid bounded on one side by a plane surface and loaded along a line on that surface, the stress (y) on an element on the normal through the middle point of the line varies inversely as its distance (x) from the surface. The formula thus arrived at was—

$$y = 0.64 \frac{P}{x},$$

whilst for a finite beam, centrally loaded, the author's experiments gave—

$$y = 0.726 \frac{P}{x}.$$

The experiments were made on glass beams mounted in a steel straining-frame, and placed between the crossed Nicols of a polariscope. Steel rollers, 2 m.m. in diameter, served as supports, and the central load was applied by a screw acting on a roller of similar diameter. Deflections of the beam were measured by a micrometer screw, at a point opposite the central load, and traversing screws enabled the whole frame to be moved so as to bring any portion of the beam in the field of view. Circularly polarised light was sometimes used, and a micrometer eyepiece served to measure the distances between interference fringes produced by loading. By carefully chosen experiments the author had shown that if a beam of glass be laid on a flat surface, and loaded across its upper surface, the shear at any point on the normal at the point of contact of the load is inversely proportional to the distance from the point of contact. In the first experiment the crossed Nicols were set at 45° to the axis of the loaded bar; a quarter-wave plate was then placed between bar and the analyser, and the position of the black spot at the point where the effect of the shear on the polarised light was equal, and opposite to that produced by the quarter-wave plate, was noted. A second quarter-wave plate was then superposed on the first; the black spot moved upwards to a point where the shear was double that at the first position. This position having been determined, one quarter-wave plate was removed, and the load diminished until the original spot moved up to the second position, and the processes repeated.

By this means a series of positions, at which the shears were in the proportions 1, 2, 4, 8, &c., were determined. Plotting the results showed the curve connecting the shear and the distance from the point of contact to be hyperbolic. Other experiments showed that the shear at any point was proportional to the load. By maintaining a constant load and measuring the distances between the interference fringes below the point of contact the hyperbolic law was confirmed.

The effect of bending a beam is, according to hypothesis, to put the upper portion in longitudinal compression, and the shear (vertical stretch) varies as the distance from the centre of the beam; the shear due to surface loading is a vertical squeeze, and, as shown above, varies hyperbolically. When, therefore, the beam is subjected to both actions, the straight line representing the bending strain may intersect the hyperbola representing the shear due to surface loading in two points, and, since at the corresponding points in the central section the shears are equal and opposite, the elements are only subjected to voluminal compression, and will exert no birefringent action. Hence, when viewed through crossed Nicols, black spots will be seen on a white field. Keeping the load constant and diminishing the span should cause the spots to approach each other, and when the line is tangential to the hyperbola the spots coincide. These deductions were confirmed by experiment, and it was found that, for a span of less than four depths, no point of zero shear exists on the central section. The strains in beams subjected to surface loading were thus shown to be of a character different from those usually assumed, the neutral axis, instead of coinciding with the axis of the beam, being lifted up in the centre, and its shape depending on the load and span.

Other ingenious and interesting experiments on beams were described, in some of which the lines of principal stress were mapped out. Remarkable results were obtained, showing that, although the tension lines given by Rankine and Airy are nearly correct, the curves of compression may be very different and have very curious shapes.

Prof. PERRY thought the local loading effect would not be so important in long beams, and inquired whether, in ordinary test-pieces, local loading would affect the breaking strength. He also asked what effect the fact of the load making contact over a surface, instead of along a line, would have on the results; and in reply Prof. CARUS-WILSON said the effect was to raise the asymptote of the hyperbola, representing the surface loading stress, above the surface of the beam.

On "Pocket Electrometers." By C. V. BOYS, F.R.S.

This communication described modifications of electrometers adapted for portability. As quartz fibres increase the delicacy and diminish the disturbing influences affecting instruments, much smaller controlling forces can be employed than when silk is used for suspensions. He had, he said, pointed out some time ago the great advantages arising from making galvanometers small. Applying similar reasoning to electrometers, he remarked that making an instrument one-tenth the size of an existing

one reduced the moment of inertia of the needle to $\frac{1}{10^3}$

—whilst the deflecting couple for given potentials would only be one-tenth of its former value. The small instrument would, for the same periodic time, be 10,000 times more sensitive than the large one, provided the disturbing influences could be reduced in the same proportion. This, however, was not ordinarily possible, for any method of making contact with the needle—such as by a fine wire dipping into acid or mercury—prevented very small controlling forces being used. Still, by suitable devices, a large proportion of the full advantage could be obtained; a freely suspended needle without liquid contact was essential to success. The first instrument described was one in which the needle was cylindrical, contiguous quarters being insulated and connected to the opposite

ends of a minute dry pile placed within the needle; opposite quarters were then at the same potential, and at a different potential to the other pair of quarter cylinders. This was suspended within a glass tube silvered on the inside, and divided into four parts by fine longitudinal lines. In such an instrument the needle and quadrants are reciprocal, and the deflection depends on the product of the difference of potential between the quadrants and that between the parts of the needle. Owing to the dry pile not being constant the instrument was found unreliable, but when working at its best a Grove cell would give 30 or 40 m.m. deflection. The next step was to make a cross-shaped needle of zinc and platinum, and rely on contact electricity to keep the parts of the needle at different potentials. This bold experiment proved remarkably successful, for the instrument was very sensitive. A disc-shaped needle, with quadrants alternately zinc and platinum, was then employed, and by this a small fraction of a volt could be measured. The weight of the disc was only 1-20th of a gramme, and the instrument could be turned upside down or carried about in the pocket with impunity. Another small instrument, with the stationary quadrants of zinc and copper, was exhibited, and by rotating them through an angle of 90°, so as to bring them in a different position relative to the parts of the needle, a deflection of several degrees of arc was produced.

In the course of his remarks Mr. Boys made several suggestions relating to Ballistic Electrometers and Electrostatic Siemens' Dynamometers, and pointed out the possibility of instruments, such as he had exhibited, being of use in elucidating the obscure points in connection with so-called "contact electricity."

The PRESIDENT complimented Mr. Boys on the beautifully simple and remarkably sensitive electrometers exhibited. He remembered that some years ago Mr. Gordon made a very small electrometer, but its insulation was insufficient for electrostatic work. He agreed with Mr. Boys as to the advantages of small instruments, providing sparking across or tilting of the needle could be prevented. On the other hand, he thought the use of small potential differences on the needle was a step in the wrong direction, when great sensibility was required.

Prof. PERRY asked if the needle could not be kept charged by occasional contacts with a charged acid cup.

Mr. Boys said he had originally intended using a fairly highly-charged needle, but had not yet done so. He also suggested that an electrometer of very small capacity might be made by reducing the quadrants surrounding a disc needle until they became like small tuning-forks.

A paper on "Electrification due to the Contact of Gases with Liquids," by Mr. J. Enright, B.Sc., and one on "The Expansion of Chlorine by Heat," by Dr. Arthur Richardson, were taken as read.

The following correction should be made in the report of the meeting on June 12th:—For the first sentence in Mr. Blakesley's remarks on Dr. Lodge's experiments, substitute—

Mr. BLAKESLEY asked whether the pitch of the resonant jars altered when the distance between the circuits was varied, for according to theory the mutual induction should diminish the self-induction and cause the oscillations to be more rapid.

The Action of Nitric Acid at Different Strengths and Temperatures upon Iron.—Henri Gautier and G. Charpy.—Nitric acid attacks iron at every degree of concentration, but the action may take place in two different manners, the one rapid and attended with an escape of gas, and the other slow and without a production of gas. The existence of these two modes of action explains very simply the phenomenon known as the *passivity of iron*, which corresponds not, as it has been hitherto supposed, to the absence of all action, but merely to a slow action without the liberation of gas.—*Comptes Rendus*, cxii., 25.

NOTICES OF BOOKS.

Photography Annual. A Compendium of Information upon Photographic Matters, and the Annals of Photography for the Past Year. 1891. Edited by HENRY STURMEY, F.S.Sc. London: Iliffe and Son.

THE number of persons who occupy themselves more or less seriously with photography is something altogether exceptional. In the windows of the opticians, cameras and their accessories seem to have displaced all other kinds of apparatus. Photographic societies have sprung up even in country towns where the talk of the natives has hitherto been almost exclusively of bullocks. Scientific societies, Young Men's Christian Associations, and even one or two "Literary and Scientific" organisations, have their photographic sections. We can only hope that Science will be benefitted by this devotion to an art which links itself in many ways not merely with chemistry and physics, but with astronomy and biology.

The goodly volume before us is not confined to matters which interest the average taker of portraits, but comprises much valuable matter on actinometry and photometry; on that grand vision of the future, photography in colours; on spectrum photography; and on astronomical photography, accompanied by a number of fine prints of the moon in different phases. But we do not find any special record of progress in the application of photography to micro-biological investigation.

We notice a very appropriate utterance of one of the contributors, *vis.*, that it "is not the true function of any art process to ape the productions of any other process." We must not regard it as high praise if we are told that "a photograph looks more like a sepia drawing than a photograph."

An essay on photographing animals is spoiled by the introduction of a phrase which is one of our most unfortunate "insular peculiarities." The writer, though a F.Z.S., speaks of the love or fear men bear towards the *dumb* creatures around them.

The paper on "Naturalistic Photography" is followed by its antidote in the shape of "Musing on some Recent Mistakes." The writer is justly severe on a school of artists, whether with camera or brush, who "cannot represent a girl feeding a dove, or picking a bunch of grapes, without giving her an expression of unutterable woe."

A paper headed "My Lantern" is a severe critique on dissolving views in any shape or form. They may do, he thinks, for "Sunday-school meetings, tea-fights, or for Temperance lectures." But, *minus* of course the dissolving, camera views are the best means of illustrating scientific or educational lectures. How poor, in comparison, is the "drawing lecture," where a sensational speaker strives to reproduce some animal or vegetable structure by dint of a black board and a piece of chalk!

The advertisements, introduced in the American manner among the text, are so numerous that the would-be purchaser is puzzled no less than the would-be reader.

Of the illustrations some are beautiful. But we are sorry to meet with our old enemy, "Portrait of a Lady," which, with the accompanying bore, "Portrait of a Gentleman," make the Royal Academy Exhibitions to many persons anything but "a joy for ever."

"Goring Church" makes as near an approach to the effect of reflections in a river as can be hoped for in case of water which is not absolutely at rest. The "Night-blowing Cereus" is a novelty; the plant is cheated into being taken by the instantaneous process. The "Silver-cup Picture" is probably suffering from face-ache. The "High Tor, Matlock," would have been more pleasing if the scenery had not been suffering from an inflection of snow.

"Miss Elsie" is a clever likeness, but the damsel herself seems to be in a wintery frame of mind.

The illustration of the collotype "In the West Indies" is excellent in its execution, but it would have been easy to find in most of the Antilles a more fascinating landscape.

To find a book of a thousand closely printed pages offered at such a low price is indeed a sign of the times, and is a fresh proof of the widespread interest taken in photography.

The Pocket-book of Mensuration and Gauging, &c.; for Revenue Officers, Brewers, Spirit Merchants, &c. By J. B. MANT, Inland Revenue. Second Edition, revised. London: Crosby Lockwood and Son.

THE author, in his Preface, announces that he has intended to furnish not a text-book, but an aid to memory when bulkier works for reference are not at hand.

This Pocket-book, from its intensely technical nature, is scantily intelligible to persons who have neither been trained for the Inland Revenue service, nor brought up to brewing, distillery, and the sale of excisable liquors. It contains an account of logarithms; of the slide-rule; method of alligation; a description of the hydrometer and saccharometer used by the Revenue; rules for blending, mixing, and reducing spirits; the chemical formulæ of the distillers' raw materials and products; instructions for finding the area of certain figures; the mensuration of solids. Then follow instructions for gauging stills; ullaging; directions—rather rough—for taking the specific gravity of a solid; beer gravity tables; beer duty calculator; tables of weights and measures, both English and metric; original gravity tables. Lastly come particulars of excise licences.

How do I Stand? being Hints and Directions in Book-keeping and Balancing for Retail Chemists. By GEORGE WEDDELL. Newcastle-on-Tyne: Mawson, Swan, and Weddell.

THE title of this little book, as it appears on the outside, led us to suppose that we had before us a treatise on the mechanism by which man is enabled to maintain the erect attitude. On opening the book we found it to be a manual of book-keeping, specially adapted for the guidance of the pharmaceutical profession, who, if the author is to be believed, have somewhat neglected this department of their business.

In the introductory portion of the work an attempt is made to answer the question why pharmacists do not become rich in the same proportion as drapers, &c.? To this query the writer replies, that it is "because they do not carry on their business on the same common-sense principles that others follow." Our opinion—whatever it may be worth—is that the pharmacist of necessity carries on his operations on a limited scale. People do not stroll into a pharmacist's shop to look round and see if there is anything they fancy. They buy medicines simply if they need them. Further, as far as the law allows, they are shamefully encroached upon by other tradesmen, especially by the monopolist drapers of the present day. At present any person can sell poisons, if only made up as a "patent," without any knowledge or care about their properties, without any caution given to the customer, and without any responsibility in cases of accidents.

Appendix to the Report of the Minister of Agriculture. Experimental Farms for 1890. Ottawa: Brown and Chamberlin, Queen's Printers.

THIS work comprises special reports of the director, the agriculturist, the horticulturist, the chemist, the entomologist and botanist, the poultry manager, and the superintendents of the four experimental farms.

The director makes the suggestive remark that "a large proportion of agricultural products appear to have a life-

period, some short, some long, after which their vigour or vitality becomes gradually impaired until their cultivation can no longer be continued with profit." He shows that, by a delay of one week in the time of seeding, the farmers of Ontario may lose 2½ million dollars on the barley crop alone.

The fruit-growing capacity of the Dominion is not as yet sufficiently estimated in England. Even in grapes it may successfully compete with the European continent. From 400 to 500 tons of grapes were shipped last year from "small stations in the Niagara district."

Varieties of apples, pears, and plums, of Russian origin, seem to succeed well.

Attention is being wisely given to planting forest trees on the plains, where their shelter will be of the highest value, not merely to fields and orchards, but to the stock-yards and the homes of the settlers. Wind is, perhaps, the greatest enemy to horticulture.

As fungicides salts of copper have proved very successful, but further experiments will be needed to decide what proportion is most deadly to fungi and least harmful to the trees themselves.

The chemist regards potash and phosphoric acid as the most important mineral constituents of a soil, and lime as the principal of "the inorganic elements of minor importance." He recognises lime (in the state of carbonate) as taking part in the process of nitrification. An excess of nitrogen, he considers, "promotes a rank growth of straw." Gypsum he finds of especial value for leguminous plants—a result which agrees with English practice.

For dressing seed-wheat, in order to destroy smut, ferrous sulphate seems much preferable to copper sulphate, as the latter was found to impair the vitality of the seeds to a serious extent, 26.5 per cent.

The Department of Agriculture offers to farmers to analyse their well-waters freely if they will pay for the carriage of samples. It appears that out of ten samples only three could be reported safe to drink.

A curious fraud has been devised for the injury of bee-keepers. "Foundation-comb" is a common article of sale beyond the Atlantic, as it saves the bees much time and labour. But the wax used for this artificial comb is largely adulterated with paraffin. As this article melts at a much lower temperature than genuine wax, in hot weather the comb breaks down; the honey is spoiled, the young brood smothered, and the bees smeared with paraffin to their disgust and injury.

From the report of the entomologist we learn that injurious insects are a tax of 10 per cent on all farm produce. In many seasons the loss will, we fear, be much greater.

The House Surgeon, or the Doctor at Home. Containing Instructions for the Prompt Treatment of Accidents and Emergencies before the Arrival of Medical Aid. By the late ALFRED SMEE, F.R.S., Surgeon to the Bank of England. Compiled specially for the Accident Insurance Company, Limited. London: The Accident Insurance Company, Limited.

As regards the methods of treatment here advised, only the practical physician or surgeon is, in most instances, competent to form an opinion. In the instructions for the treatment of poisoning cases, two of the most formidable substances, chrome and barium, are overlooked. This is the more to be regretted since both these substances are largely used in the arts. For any soluble compound of barium, Epsom salts or sulphate of soda should be used. For chrome there is probably no remedy but the prompt use of the stomach-pump. For all cases where strong coffee is recommended, it must be remembered that the ground coffees sold in tins, under the mendacious names of "Coffee as in France" or "French Coffee," will not be of the slightest use.

The caution to policemen not to treat persons who are

in a fit, or who have been stunned, as if drunk, is very needful. The commencement of fevers and the approach of apoplexy often cause the patient to walk unsteadily.

The application of "laundresses' blue" for the stings of wasps, &c., is the more mysterious as this article has completely altered its nature. Formerly it was smalts,—a preparation of cobalt, rarely free from a trace of arsenic,—or sometimes a preparation of indigo. Now it is artificial ultramarine. It is scarcely conceivable that substances of such different chemical composition should have the same physiological action. Caustic ammonia, which is in fact recommended in an earlier part of this pamphlet, will be found preferable if the injury is not on or near the eye.

Alkali Works Regulation Act, 1881. Twenty-seventh Annual Report on Alkali, &c., Works. By the CHIEF INSPECTOR. Proceedings during the Year 1890, presented to the Local Government Board and to the Secretary for Scotland. London: Printed for Her Majesty's Stationery Office, by Eyre and Spottiswoode.

THE inspection of alkali works, or, as we may rather say, chemical works, is still carried on satisfactorily. The Chief Inspector states that the analysis of the air or gases escaping up the chimney is now recognised as an essential part of the daily duty. The total number of works under inspection is 1034, of which 133 only are alkali works strictly speaking. The amounts determined are remarkably uniform, "agreeing year after year within small fractions of a grain."

During the year 1890 there has been no prosecution for any infraction of the Act, and, what is more, no complaints have come in from farmers and others as regards damage done by noxious vapours. To this satisfactory state of things there is one only exception. The Chance process for utilising the sulphur present in the tank waste has encountered "unexpected difficulties and partial disappointment." Many modifications of the original process have been devised, and have been under certain circumstances successful. The Chief Inspector hopes that ultimately neither hydrogen sulphide nor sulphur dioxide will escape into the air.

The salt trade, as compared with 1888, has fallen off by 12 per cent, owing to the enhanced price of fuel. The total salt consumed in the United Kingdom in 1890, in the alkali manufacture has been 885,029 tons, of which 632,769 tons have been used in the Leblanc process.

The production of sulphate of ammonia has risen from 122,785 tons in 1888 to 134,257 tons in 1890. This increase would doubtless have been greater if the yield from the iron and coke works had not been interfered with by the prolonged strike in the iron trades.

Improvements have been attempted in the process for recovering the ammonia, &c., liberated in coke ovens. The admission of air, however, partly destroys the ammonia and modifies the other products. The Mond process seems to have but a doubtful future unless coal becomes cheaper and ammonia commands a higher price.

The combined alkali process of Parnell and Simpson, we are told, has not fulfilled the hopes of its promoters, and the experimental work is for the present abandoned. On the other hand, Dr. Affleck, the Widnes inspector, considers that the Haddock and Leith process has some decided advantages over the Chance, the Gossage, and the Solway processes.

It is rather a novelty to find black coal smoke referred to in the reports under the Alkali Act. It is evident that the smoke escaping from chemical works is a trifle in comparison with that generated by iron works, by locomotives on railways, and by marine engines on navigable rivers and in harbours.

As regards the smoke from dwelling-houses, Mr. Fletcher states that he has lived for five winters "in a house where no bituminous coal was burnt, and no contribution was made to the smoke of London." This is

so far very well; but if even half the householders in London were to adopt this expedient the price of non-bituminous coal would quickly reach a prohibition point.

As regards the manufacture of cement we find a remark which is no longer applicable. The manufacture is said to have been "very brisk." It is now exceedingly slack, partly from rampant competition and partly from strikes and rumours of strikes. Some of the professional agitators think themselves entitled to interfere in the management of all chemical works, and it is now difficult to discharge a drunken or dishonest workman without the threat that the workmen will be "called out."

CORRESPONDENCE.

ON THE PRODUCTION OF MUSICAL NOTES FROM NON-MUSICAL SANDS.

To the Editor of the Chemical News.

SIR,—I have now succeeded in producing musical notes from sand that was never before musical, and am also able to produce similar results from those mute, or "killed," musical sands which have been temporarily deprived of their musical properties.

Full details will shortly be made public, but in the meantime some may be interested to know that all my experiments have been conducted on the principles involved in the theory which I propounded in 1888 to account for the emission of musical sounds from such sands, and that the results obtained appear to demonstrate indisputably the applicability of this theory.—I am, &c.,

CECIL CARUS-WILSON.

Bournemouth, June 27, 1891.

[A short time ago I had the pleasure of witnessing Mr. Carus-Wilson's experiments with musical sands—sands originally musical, musical sands which had been killed and then revived, and sands originally mute which had had the gift of music conferred on them. Mr. Wilson hopes soon to be prepared to publish his experiments and the explanation of the phenomena in detail.—W. C.]

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxii., No. 25, June 22, 1891.

The Electrolysis of Barium Chloride, either Pure or Mixed, with Sodium Chloride.—C. Limb.—The author's experiments were undertaken with a view of obtaining metallic barium. But neither from pure barium chloride nor from the mixture of barium and sodium chlorides has he been able to obtain at the cathode even the smallest quantity of the metal. Chlorine, however, was evolved in abundance, and it appears probable that there is formed a barium or a sodium sub-chloride, or possibly a combination of both.

Calculation of the Boiling-Heat of any Liquid whatever, under any Pressure.—G. Hinrichs.—A purely mathematical paper which does not admit of useful abridgment.

Action of Heat upon the Solutions of the Salts of Chromium Sesquioxide. Green Chromium Salts.—A. Recoura.—The author concludes that within the limits of concentration in which he has been able to operate a

dissolved chromium sesquisulphate is split up completely under the influence of heat into free sulphuric acid and a soluble basic sulphate of a perfectly definite composition, $2\text{Cr}_2\text{O}_3 \cdot 5\text{SO}_3$. It is derived from 2 mols. of sulphate, which lose 1 mol. of acid, and it contains a modified oxide which is unable to fix a further quantity of acid. This modified sesquioxide cannot exist in a free state, and when it is precipitated by decomposing the green sulphate with an alkali it is split up and the precipitated oxide is a new modified oxide, 1 mol. of which takes up only 2 mols. of sulphuric acid.

Researches on Osmium: Osmiamic Acid and the Osmiamates.—A. Joly.—The author has resumed the study of osmium acid—a compound containing both nitrogen and oxygen, discovered by Fritzsche and Struve in 1847. He prepares the potassium salt of osmium acid by dissolving crystalline osmium tetroxide in potassa (OsO_4 100, KOH 100, water 50). To the liquid, which is kept at 40° , he adds 40 c.c. of caustic ammonia. In a few moments the brown liquor is deposited and deposits a yellow crystalline precipitate of potassium osmiumate. When the decolouration is complete and the liquid is cold he decants, washes the salt with iced water, and dissolves it in boiling water. It crystallises on cooling in fine quadric octahedra. It is important to avoid an excess of ammonia, which would leave the potassium osmiumate mixed with a very unstable ammoniacal salt. The composition of the potassium salt is expressed by the formula $\text{OsO}_2\text{NK} + 2\text{H}_2\text{O}$. Osmiamic acid may be approximated to the nitroso-compounds of ruthenium which the author has previously described, RuNOCl_3 , $\text{RuNO}(\text{OH})_3$. If we admit the existence of a compound $\text{OsNO}(\text{OH})_3$, osmium acid will be its first anhydride.

On the Alkaline Zirconates.—L. Ouyard.—The author has obtained a lithium zirconate by fusing lithium chloride with zirconia. He assigns to the crystallisation obtained the formula LiOZrO_2 . Zirconium silicate behaves like an acid.

On Silicon Bromoiodides.—A. Besson.—The author has obtained and examined $\text{Si}_2\text{Br}_2\text{I}$ —a colourless liquid which distils at 192° , and which, on refrigeration, presents a very distinct phenomenon of superfusion. The compound $\text{Si}_2\text{Br}_2\text{I}_2$ is a white solid which melts at $+38^\circ$, and distils at 230° – 231° . The compound $\text{Si}_2\text{Br}_2\text{I}_3$ is a white solid melting at 53° and distilling at 255° . In a future paper the author will describe the preparation and the properties of boron phosphide.

On the Cyanogen Compounds of Magnesium.—Raoul Varet.—The author here describes the double magnesium-mercury iodiccyanide and the corresponding bromocyanide. The action of magnesium iodide upon mercury cyanide yields a compound of magnesium cyanide and mercury iodiccyanide; the action of magnesium bromide upon mercury cyanide yields a compound of the same order.

Action of Sodium Benzylate upon Camphor-Carbonic Ether.—J. Minguin.—Not adapted for abstraction.

Comparative Influence of Iron Sulphate and Calcium Sulphate upon the Retention of Nitrogen in Bare Soils, and on Nitrification.—P. Pichard.—According to the author gypsum is more effective than ferrous sulphate in preventing the escape of nitrogen and in favouring nitrification.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., Part 2, No. 586.

Treatment of Uranium Residues.—Dr. Laube (*Zeit. Angewandte Chemie*).—The uranic residues are preserved in a large jar, the supernatant liquid being from time to time poured away until the pasty deposit containing the uranium fills about two-thirds of the vessel. It is then heated to ebullition, either by a current of steam passed into the vessel or in an iron pan over a naked fire, adding from time to time crystals of soda until the uraniferous

portion of the precipitate appears dissolved. Without filtering he pours into the liquid when cooled so much ammonia that its odour may be distinctly smelt, and then a mixture of equal parts of ammonia and magnesium sulphate, so as to throw down all the ammonium magnesium phosphate. During this last treatment the liquid must be carefully stirred. After settling for twelve hours the liquid is drawn off with a syphon, and the residue washed repeatedly with ammonia water. These liquids are passed through the filter which receives the precipitate. The alkaline liquids are placed in large vessels half-filled, and are neutralised with sulphuric or hydrochloric acid, and the carbonic acid is totally expelled by boiling. The uranium is then expelled by means of ammonia, in the form of ammonium uranate. The precipitate is easily washed at first by decantation with hot water. Afterwards it is necessary to add a small quantity of a salt of ammonium, as the precipitate otherwise would only subside imperfectly.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Bleaching Fat.—Will any reader kindly inform me how to bleach bone fat white?—ENQUIRER.

Separation of Cotton from Wool.—I should be glad if any of your readers could give me any information about the process for the carbonising of woollen rags containing cotton, and if there has been any book published on this subject.—G. L.

Copper Antimonide.—In the *Chem. News* for April 6th, 1888, (vol. lvi., No. 1486), we see a chapter on the "Occurrence in Nature of Copper Antimonide," wherein it states that there is a deposit of this mineral at Mytilene. We believe we have discovered a process that will treat this ore successfully, commercially; and our object in writing is to ask if you can by any chance put us in communication with Mr. Melcon, who is mentioned in the article as having sent over some samples of the ore.—BOWEN, SCOTT, AND WESTERN.

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PRACTICAL WORK IN ORGANIC
CHEMISTRY. By F. W. STREETFIELD, F.I.C., &c., Demonstrator of Chemistry at the City and Guilds of London Institute's Technical College, Finsbury. With a Prefatory Notice by Prof. R. MELDOLA, F.R.S., F.I.C.

London: E. and F. N. SPON, 125, Strand.

BRITISH ASSOCIATION FOR THE
ADVANCEMENT OF SCIENCE, 22, Albemarle Street,
London, W.

The NEXT ANNUAL GENERAL MEETING will be held at
CARDIFF, commencing on Wednesday, August 19.

President Elect—

WILLIAM HUGGINS, Esq., D.C.L., LL.D., F.R.S., F.R.A.S.

NOTICE TO CONTRIBUTORS OF MEMOIRS.—Authors are requested to give notice before August 1st of their intention to offer Papers.

Information about Lodgings and other local arrangements may be obtained from the Local Secretaries, Bank Buildings, Cardiff.

G. GRIFFITH, Assistant General Secretary.

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working Chemist, with a good Knowledge of the Manufacture of Glue, Gelatine, Oils, &c. One who speaks Spanish preferred. Salary £300 per annum.—Address, stating age, qualifications, &c., to "P. C., 2," care of Street's, Cornhill, London.

THE CHEMICAL NEWS.

VOL. LXIV., No. 1651.

NOTES ON SOLUTIONS OF ARSENIUS OXIDE.

By E. GODWIN CLAYTON.

THE following results of experiments made by me with arsenious oxide (As_2O_3) may be recorded, for the purpose of comparison with the results of other workers:—

Cold Aqueous Solutions.

1. Arsenious oxide shaken with distilled water (temp. $15^{\circ}C.$), at intervals of half an hour, for a period of four hours. Quantity dissolved, 0.118 grm. in 100 grms. of water, or 1 part in 847.

2. Arsenious oxide shaken with distilled water (temp. $15^{\circ}C.$), at intervals of twenty minutes, during a period of six hours. Quantity dissolved, 0.269 grm. in 100 grms. of water, or 1 in 372. Specific gravity of this solution, 1.0023. [Buchner (*Z. Ph.* [3], 1, 421) gives the strength of a solution prepared from the crystallised oxide by digestion for some days at $15^{\circ}C.$ as 0.28 per cent, or 1 in 357.]

3. Arsenious oxide shaken with water (temp. as before) at frequent intervals during four days. Quantity dissolved, 0.99 grm. in 100 grms. of water, or 1 in 101. Specific gravity of solution, 1.0079.

None of the above solutions deposited arsenious oxide when left to stand for several days.

Hot Aqueous Solutions.

4. Arsenious oxide boiled with distilled water for one hour; solution gradually cooled and allowed to rest for twenty-nine hours. Quantity of As_2O_3 dissolved, 2.23 grms. in 100 grms. of water, or 1 in 45. A duplicate experiment gave 2.22 grms. Specific gravity of solution, 1.0177. [Buchner (*op. cit.*) gives 2.18 per cent as the strength of a solution saturated at $100^{\circ}C.$, and cooled to 15° .]

5. Arsenious oxide boiled with distilled water for four hours. Quantity found in solution in 100 c.c. of liquid, measured at about 93° , 9.52 grms., or 1 in 104.

6. A portion of the same solution allowed to cool and stand for an hour and a half. Quantity still in solution, 8.24 grms. in 100 c.c., or 1 part in 12.

7. Another portion of the same solution left at rest for 454 hours. Quantity remaining in solution, 3.28 grms. in 100 c.c., or 1 part in 30. Specific gravity, 1.0254.

8. Another portion allowed to stand for ninety hours. Quantity in solution, 3.21 grms. in 100 c.c., or one part in 31.

In experiments 6, 7, and 8, the separated As_2O_3 formed a crystalline film on the sides and bottom of the containing vessel, as well as a crust covering the surface of the liquid. Finely-divided crystallised As_2O_3 was used in every case. The results obtained show the large influence which the time of digestion and frequency of shaking have upon the quantity of the oxide dissolved. By prolonged digestion, with frequent agitation, it is evident that a cold aqueous solution, of considerably greater strength than that obtained by Buchner, can be prepared. The solution made in experiment 3 is seen to be of about 1 per cent strength. The solutions prepared with boiling water, and afterwards cooled and allowed to stand, as in experiments 7 and 8, were also stronger than Buchner's. In "Watts' Dictionary," First Edition, vol. i., p. 374, it is stated that a hot saturated solution, afterwards cooled, retains 1 part in 30 of the oxide—my own results corroborating this.

The minute crystals obtained on evaporating small quantities of the aqueous solutions to dryness were seen under the microscope to be, chiefly, unmodified regular

octahedrons and cubo-octahedrons, together with what appeared to be triakis octahedrons and various tetrahedral forms.

Alkaline Solutions.

9. Arsenious oxide was boiled with excess of an aqueous solution of potash (1 : 10) for three hours. The quantity of oxide dissolved was estimated in 100 c.c. of the solution, measured hot, and found to be 34.08 grms., or about 1 in 3.

10. A portion of the same solution was allowed to stand for twenty-four hours. Quantity of As_2O_3 now remaining in solution, 14.29 grms. in 100 c.c., or 1 in 7. Well developed, transparent, and lustrous crystals of the oxide had been deposited in the flask.

ON THE

NATURE OF SOLUTION.

By J. ALFRED WANKLYN and W. J. COOPER.

THE solution of sugar by water affords one of the simplest and most typical examples of solution. The following facts have been ascertained by us:—A quantity of sugar in coarse powder was placed in a half-litre flask, and water poured into the flask until the half-litre mark was reached; and the observation was made that no contraction or expansion takes place during the dissolving of the sugar.

In another experiment we weighed out 51.50 grms. of sugar, dissolved it in water in a 100 c.c. flask, filled up accurately to the mark, and weighed.

	Grms.
Weight of the 100 c.c. of sugar solution ..	119.082
Sugar	51.50
Water	67.582

Taking the sp. gr. of sugar at $20^{\circ}C.$ as 1.590, the volume of the sugar employed was 32.4 c.c. It is, therefore, accurately true that when sugar dissolves in water the volume of the solution is equal to the sum of the volumes of sugar and water. We attach much importance to this observation. Many far-reaching consequences flow from it. Each gramme of sugar as it enters into the 100 c.c. of solution raises the weight of the solution to the extent of 0.371 grm., and displaces 0.629 grm. of water.

The customary tables of specific gravities of solutions of different strengths are so constructed as to mask the simple relation between the strength and the specific gravity. By changing them so as to set out the specific gravities corresponding to the number of grms. of sugar in 100 c.c. of sugar solution, the regularity becomes manifest. Thus:—

No. of grms. of sugar in 100 c.c. of sugar solution.	Sp. gr.
1	1.00371
2	1.00742
3	1.01113
4	1.01484
5	1.01855
10	1.03710
20	1.07420
30	1.11130
40	1.14840
50	1.18550

The value 0.371 is the increment of specific gravity due to 1.000 grm. of sugar existing in the solution. It may be termed the increment coefficient = i .

When sugar dissolves in water there is neither rise nor fall of temperature—it is a pure and quite unmixed example of the phenomenon of solution.

Salt and Water.—We placed 73.7 grms. of salt in a half-litre flask, added water up to the half-litre mark, and made our observations. As the salt dissolved the level of the liquid fell, and when the solution was complete the contraction had become 9.0 c.c. The temperature was

almost absolutely unchanged. The specific gravity of the salt solution (containing 14.74 grms. salt in 100 c.c. of solution) was 1.0988. The increment coefficient $i = 0.670$.

The water displaced by 1 grm. of chloride of sodium is 0.330. Therefore the liquid density of chloride of sodium is $\frac{1}{0.33} = 3.03$.

By experiment we found the specific gravity of solid chloride of sodium to be 2.13 at 17° C. The contraction which salt undergoes when it passes into solution is consequently very marked. There are two obvious ways of looking at this contraction on liquefaction—(1) it may be like the contraction when ice melts; (2) it may be due to chemical combination between the salt and the water. Which of these views is correct, or, indeed, whether both may be right and the contraction be partly the ice case and partly due to chemical combination, remains to be ascertained. Starting, however, with the liquefied salt we may ask does it behave like sugar?

Is the value i constant for all degrees of concentration? The answer returned by experiment appears to be "nearly constant but not quite constant." When the solutions are very dilute the value of i rises slightly. Thus with a solution containing 1.474 grms. salt per 100 c.c. of solution, the value of $i = 0.709$.

It is, however, to be noted that the departure from what may be called the theoretical density is very small indeed, viz. :—

Theoretical density	1.00987
Experimental „	1.01048

Bromide of Sodium.—We have taken the specific gravity of the solid salt; we find it to be 3.20 at 16° C. When this salt dissolves in water there is a little contraction, but not so much as in the case of the chloride.

A solution of the bromide containing 50.20 grms. per 100 c.c. of solution has a specific gravity of 1.3722 at 15° C. ∴ $i = 0.741$.

A solution containing 10.04 grms. per 100 c.c. of solution had a specific gravity of 1.07606. Therefore $i = 0.757$.

In the case of the bromide i is very nearly constant for different strengths of solution.

Iodide of Sodium.—Specific gravity of solid at 16° C. we found to be 3.31. A solution containing 41.01 grms. per 100 c.c. of solution had specific gravity 1.3021 at 16° C. Therefore $i = 0.737$.

A solution containing 8.202 grms. had specific gravity 1.06128. Therefore $i = 0.747$. In this instance i is almost absolutely constant for different dilutions.

Anhydrous Chloride of Barium.— BaCl_2 , specific gravity 3.13 (solid) dissolves in water with evolution of heat.

A solution, strength 18.372 per 100 c.c. of solution, specific gravity 1.14610, $i = 0.795$.

Anhydrous CaCl_2 , specific gravity (solid) 1.94, $i = 0.675$.

Sulphate of Magnesia.—Specific gravity of the crystals $\text{MgOSO}_4 \cdot 7\text{H}_2\text{O}$ 1.70. This case is interesting.

The specific gravity of a solution containing 62.1 grms. of crystals in 100 c.c. was 1.271.

In dissolving in water, therefore, the crystals contracted very slightly (only about $\frac{1}{15}$). If we regard the solution as a solution of anhydrous MgOSO_3 in water, we have the value $i = 0.890$ and 0.110 as the water displaced by one grm. of MgOSO_3 ; and as a further consequence $\frac{1}{0.110}$

or 9.09 as the fluid density of MgOSO_3 . Manifestly such a density is absurd.

It is proved, therefore, that aqueous solution of sulphate of magnesia is a solution of the crystals—not of the anhydrous salt, and the value of i for the crystals is nearly the same as i in the case of sugar.

Our view of solution is that it is simple and regular, as illustrated by sugar. It is modified by chemical changes, and its regularity is masked.

Laboratory, New Malden, Surrey.
July 13th, 1891.

RECENT INVESTIGATIONS ON THE FULMINATES.

By H. N. WARREN, Research Analyst.

THE exact nature or formulæ of fulminic acid and its compounds, owing to their extreme unstableness, even to the present time is, comparatively speaking, little known. The following experiments lately performed with these bodies, although possessed of scientific interest only, offer further contributions to our knowledge of them. On account of the extremely dangerous nature of the fulminates, necessitating the use of so small a quantity when examining them, some slight doubt naturally remains as to their exact nature. The salt used to conduct the experiments with was argentic fulminate (ordinary fulminating silver). This being dissolved in hot water and digested with copper filings was transformed into cupric fulminate; the green salt thus obtained was dissolved in water, and introduced into a tube open at either end, one extremity being closed by means of a porous diaphragm. The salt was then reduced by means of nascent hydrogen according to the usual method, namely, by connecting the same to a small Daniell's cell, the inside of the tube being provided with a platinum electrode connected with the negative end of the battery. In the course of a few hours the whole of the copper had become reduced to the metallic form, and firmly attached to the platinum plate.

The solution obtained, being thus freed from copper, was next examined, and was found to contain, besides large quantities of hydrocyanic acid and ammonia, distinct quantities of fulminic acid, evidently existing partly as the hydrogen compound and partly as ammonium fulminate. This was converted into, and further examined as, argentic fulminate by digesting the same with argentic carbonate. In every instance an explosive fulminate was re-formed, corresponding to the normal fulminate. In the next experiment cupro-ammonium fulminate was obtained by the addition of an excess of ammonia to a solution of cupric fulminate.

The deep blue crystals thus formed were, after being dried by suspending over sulphuric acid, decomposed by means of sulphuretted hydrogen. The products consisted, however, chiefly of copper sulphide, with urea and ammonium sulphocyanide.

Further, an attempt was made to combine fulminic acid with the element silicon by passing a stream of dry silicon fluoride over argentic fulminate, kept moist by means of petroleum. Large quantities of argentic fluoride were at once formed, and the escaping gas, when collected and examined by introducing a light to the same, exploded with great violence.

Although the experiments when performed by the same method yield results which closely agree, it still remains an open question whether such a compound as silicon fulminate does in reality exist. Chlorine, iodine, and bromine were also employed, but chiefly gave rise to the substance known as chloropicrin and other bodies of an allied formula.

Experiments were also performed with a view of obtaining an ethyl compound, but these require further investigation before speaking definitely of them.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

A NEW METHOD FOR THE ESTIMATION OF CANE SUGAR IN SOAP.

By J. A. WILSON.

In an examination of the best methods of determining soap adulterants, I have felt the want of a quick, rapid method, for the determination of sugar, which is frequently added to toilet soaps to the extent of 20–30 per cent.

The method of separation of the fatty acids by decom-

position with mineral acid, which converts the sucrose into invert sugar, with subsequent titration with Fehling's solution, gives fairly satisfactory results, but which are inclined to be too low owing to destruction of the invert sugar by the prolonged action of the mineral acid.

The best way of conducting the inversion process is to add to the weighed hot soap solution one or two c.c. of normal acid in excess, separate the fatty acids as quickly as possible, and carefully neutralise, then evaporate to 75 c.c. and invert the sugar by means of HCl in the usual manner; the estimation of the invert is then made gravimetrically.

In the new method we estimate the cane sugar as such by means of the polarimeter in the following manner:—10 grms. of the soap are dissolved in a beaker in 150 c.c. of water at 80°C., and a saturated solution of magnesium sulphate added drop by drop from a pipette, stirring well till in slight excess. The whole is thrown on a capacious filter, and the magnesia soap washed three to four times with hot water containing a little $MgSO_4$. The filtrate and washings, which are slightly alkaline, are treated with very dilute HNO_3 till the alkalinity is very faint. Evaporate to 40 c.c., cool, add dilute HNO_3 till just acid, then a few drops of basic lead acetate and 2 c.c. of alumina cream; dilute exactly to 50 c.c. and polarise the solution in a 200 m.m. tube. The number of angular degrees divided by 2.66 (if the rotation is for the D line) gives the grms. of cane sugar in the 10 grms. of soap taken. I have made the following experiments to prove the accuracy of the process:—

1. 10.165 grms. of a sample of transparent soap gave a solution, when diluted to 50 c.c., rotating 3.66 angular degrees for the D line, equal to 1.376 grms. sucrose, or 13.53 per cent.

2. The same soap on second test gave 13.48 per cent. The percentage as found by inversion by HCl and weighing as CuO was 13.33 per cent.

3. 10 grms. of a sample of soap containing no sugar, 2 grms. of absolute glycerol, and 1 gm. of pure cane sugar gave a solution rotating 2.55 angular degrees for the D line, which is equal to 0.96 gm., or 9.6 per cent instead of 10 per cent.

4. 10 grms. of soap (containing no sugar), 2 grms. of absolute glycerol, and 2 grms. of pure cane sugar, when treated by the above process, gave a solution, when diluted to 50 c.c., giving the rotation $(A)_D = +5.32$, the calculated activity being 5.33.

We consider these experiments quite satisfactory for all practical purposes. It will be noticed that the optical activity of cane sugar has been taken as working simply in a watery solution, whilst really we have a mixture of salts and glycerol, but the above experiments show that the rotation is not influenced to any appreciable extent by these foreign matters. The process is simple and can be worked in about two hours from the commencement.

Tottington Mills, July 7, 1891.

A NEW SOURCE FOR XYLOSE.*

By W. E. STONE and DUMONT LOTZ.

ONE of us, in applying the furfural test to a variety of vegetable materials, in search of the pentose carbohydrates, or *pentans*, found that the "cobs" of Indian corn were especially rich in these bodies.†

In the preliminary test cited, by distilling the air-dried material with sulphuric acid of 1.254 specific gravity, and precipitating the furfural thus obtained as furfuramide, the equivalent of 12 to 13 per cent of furfural was obtained. This result, which quite equals that obtained

under similar conditions from cherry gum and gum tragacanth, indicated that the corn "cobs" might compare favourably with the latter materials as a source of one or the other of the pentoses. Since the tests mentioned we have repeated the furfural determinations, making use of a method proposed by Tollens and Chalmot, and privately communicated to one of us. By this method the material is distilled with hydrochloric acid of 1.06 specific gravity; the furfural thus obtained is precipitated from acetic acid solution with phenyl-hydrazine, dried in a current of dry air at 60°, and weighed as phenylfurfurazide. In this way somewhat higher results were obtained. One distillation of the air-dried material gave 21.89 per cent furfural, and a second 22.36 per cent.

Our method of procedure was to extract the pentose carbohydrates from the material by means of strong alkalies, and then by hydrolysis convert them into the specific pentose.

Two and one-half kilos. of finely-ground air-dried "cobs" were digested, cold, with 12 litres of 1 per cent ammonia solution during about thirty hours, for the purpose of removing colouring matters. When drawn off the liquid was of a dark brown colour, but nothing was precipitated from it when several volumes of strong alcohol were added, showing that none of the gummy pentose carbohydrates had been extracted.

The residue, which was perceptibly lighter in colour than before this treatment, was next subjected to the action of a sodium hydroxide solution in order to effect solution of the gums. In his treatment of sugar-beet chips for the extraction of the so-called metapedic acid from which arabinose was first prepared, Scheibler used for this purpose quicklime.* Later, one of us by the same process obtained from the fermented residue of malt a gum which, upon hydrolysis, yielded both arabinose and xylose.†

Tollens and Allen have found, however, that caustic alkalies gave better results in the preparation of xylose from wheat-straw.‡

Accordingly, the residue left after extraction with ammonia received enough of a 2 per cent sodium hydroxide solution to cover it, and the whole was boiled during eight hours, the liquor becoming very dark coloured and mucilaginous. After standing eight hours longer the liquor was separated from the residue of fibre and insoluble matter by means of a press. Upon addition of two volumes of 95 per cent. alcohol to this liquor, a voluminous, dark brown, gummy precipitate was thrown down. This was several times washed with alcohol by decantation. Finally it was re-dissolved in a little water, to which some hydrochloric acid had been added, and then re-precipitated with alcohol. This treatment was repeated several times. The final result was an amorphous substance of light brown colour, which upon exposure to the air seemed slightly hygroscopic, and rapidly blackened. After drying over sulphuric acid this product weighed about 200 grms., or about 8 per cent of the material employed.

A small quantity of this gum was repeatedly dissolved in water and re-precipitated from an acid solution by means of alcohol, with the object of obtaining a pure ash-free product for further study. The last traces of ash were, however, very difficult to remove, and after some months the preparation still contained 0.76 per cent. Spectroscopic examination showed this ash to consist of sodium salts. Two portions of this gum yielded on distillation, respectively, 48 and 50 per cent. of furfural. This partially purified material was noteworthy for its solubility in water and its rapid discolouration on exposure to the air. The greater portion of the 200 grms. of gum was heated in a flask with 2 litres of 2 per cent sulphuric acid for twelve hours, an inverted condenser being used to prevent concentration of the acid by evaporation.

* Contributions from the Chemical Laboratory of Purdue University.

† *Am. Chem. Jour.*, 13, 73

* *Ber. d. Chem. Ges.*, 1, 58, 108.

† *Ann. Chem. (Liebig)*, 249, 243.

‡ *Ibid.*, 260, 289.

At the end of this time about 50 grms. of amorphous, insoluble matter remained in the flask. The acid liquor was filtered from this residue, neutralised with calcium carbonate, and evaporated to a thick syrup. Upon adding about three volumes of strong alcohol to this and boiling, a dark brown, tasteless gum was precipitated and removed, and the liquid after concentration yielded slowly a mass of dark coloured crystals.

After repeated washings and re-crystallisations, two successive portions of crystals were obtained, which were nearly white, sweet to the taste, and reduced Fehling's solution strongly. In all about 6 grms. of this product were obtained, or nearly 3 per cent of the 200 grms. of gum used. Probably an equal amount of sugar remained in the dark coloured and non-crystallisable mother liquors. The amount of this product obtained was disappointingly small in view of the promising preliminary indications. The syrups obtained after hydrolysis, however, contained much unchanged gummy matter, and crystallised only slowly and with great difficulty. It was also found subsequently that the extracted cobs still contained a very large amount of the furfural-producing bodies. The caustic soda had evidently extracted only a very small amount of the *pentans*, or pentose gums, which accounts for the small yield of sugar. To characterise the product thus obtained, the specific rotation was determined, and its phenylhydrazine derivative prepared. Of the two portions of crystals, No. 1 showed the specific rotation $(\alpha)_D = 19.4^\circ$; No. 2, $(\alpha)_D = 19.7^\circ$. These numbers agree with sufficient accuracy with the specific rotation of xylose— $(\alpha)_D = 18.5^\circ$ to 19° —to identify both products as xylose, and show that this was the only pentose present. The phenylhydrazine compound was prepared in the usual way, had a normal appearance and behaviour, and showed the melting-point 159° —the approximate melting-point observed for phenylxylosazon (156° — 160°). In distinction from the phenylarabinosazon, which has the same melting-point, this compound was distinctly *laevo*-rotatory, a property of the xylose derivative as shown by Fischer.*

These data add a new and, as we hope to show by a repetition of the above work, a fruitful source of xylose to those already known, and emphasize once more the reliability of the furfural test for the recognition of such materials.—*American Chem. Journal*, Vol. xiii., No. 5.

ON TERMINAL SPECTRA OBSERVED IN VACUO.

By E. E. BROOKS.

IN the *CHEMICAL NEWS*, vol. lxii., p. 230, November 14th, 1890, I gave a brief preliminary notice of these spectra in a paper on the "Phosphorescence of Lithium Compounds," and as I believe they have never previously been mentioned I now propose to describe them more fully.

Terminal spectra are of the same order as spark spectra obtained in air, their interest mainly lying in the method by which they are obtained, which is usually as follows:—

A number of small vacuum tubes are prepared, 2 or 3 inches long and half an inch diameter, one terminal being a very small plate of aluminium, not more than $\frac{1}{4}$ in. square, and usually covered on one side by a mica screen, the other terminal being either the same or a small spiral of fine wire. Some metallic salt or compound is introduced, and the tube exhausted to the required degree, and then sealed up. To use it, a little of the contents is made to rest on one of the terminals by shaking or jerking the

tube, and the terminal (made negative) is examined with the spectroscope while coil discharge is passing, lines due to the metal being then seen superposed upon the spectrum due to the gas.

I at first hoped that the method would enable me to prepare standard tubes containing salts of various metals, which would give metallic spectra as readily and permanently as vacuum tubes containing gases, and with a few metals this is possible, but with the majority the method is inferior to the ordinary spark process in air.

The metallic lines are easily distinguished from the gaseous lines seen at the same time. The latter are steady, extend the whole width of the spectrum, and are of equal brilliancy throughout; while the former flicker more or less, and often appear in flashes, and usually only extend partly across the spectrum. The C and F lines of hydrogen are almost always very strong.

It will be seen that these spectra are quite distinct from the phosphorescent spectra first studied by Mr. Crookes, which are of a totally different character, and are only visible at a degree of exhaustion much beyond the limit at which these spectra disappear.

Some fifty vacuum tubes of various designs were made and used, experiments being made with carbon terminal soaked in solutions of salts, with movable terminals with fused coatings, and with terminals of different metals. The following results were obtained, using a coil giving about 1 inch spark, which was hardly powerful enough for the work.

Lithium.—These spectra were first noticed while examining a specimen of LiNO_3 in *vacuo*. The salt was heated with a lamp until partly volatilised, a portion condensing again on the aluminium terminals of the tube. On passing the discharge, the negative terminal shone with a deep red light, which was found to give the red and orange lines very strongly. All the salts of this metal give very good results.

Sodium.—The D lines are as common an impurity in these spectra as they are in spark and flame spectra, and the reaction seems almost as delicate. Using any sodium salt, the terminal is covered by an intense yellow glow, and the D lines are always strong. A slight increase of strength in the discharge brings out the double green line, and the double red line can be seen occasionally. NaCl has a bright greenish phosphorescence in a high vacuum.

Cesium.—The two blue lines (α and β) are seen occasionally when the chloride is used, but not very readily.

Barium.— BaCl_2 gave readily a good and distinct spectrum, which remained visible in higher vacua than usual. The following lines were identified:—

6496, 6141, 5853, 5534, 4933, 4553, and (probably) 4165.

BaCl_2 phosphoresces bright greenish-blue in a high vacuum.

Calcium.— $\text{Ca}(\text{NO}_3)_2$ was used. The terminal shone with a strong red glow, and brilliantly white incandescent points broke out here and there. The orange and green bands came out very distinctly, and the bluish violet line 4226 was well seen in the flashes.

Strontium.—The chloride and nitrate were used, but with rather poor results. The red lines were almost invisible, green and blue lines were glimpsed in flashes, but the only one I could identify with certainty was the blue line 4607, which was easily seen.

Magnesium.—Using the sulphate or nitrate, the triple green lines came out strongly at times, but the effect was rather uncertain. Very intense green points occasionally seen on the positive terminal.

Zinc.—The oxide and sulphate were used. The red line 6360 was very strong, and three green lines, 4810, 4721, 4679, were also seen. ZnO phosphoresces in a high vacuum with a peculiar greenish yellow glow, and ZnSO_4 gives a bright bluish phosphorescence.

Cadmium.—With the iodide two lines came out very distinctly at 5085 and 4799. In a high vacuum the salt gave a bright light yellow phosphorescence, with traces of brown and red. Heating the salt with a spirit lamp caused a whitish coating to condense on the sides of the tube, and when the discharge was again passed, this coating shone with a very bright greenish yellow light, similar to the phosphorescence of German glass, but evidently not due to the glass of the tube, as the latter was made of lead glass.

Lead.— $PbCl_2$ was used. A good spectrum easily obtained, and for the first time metallic lines were noticed on the positive terminal. A jet of light shot out from one side of the negative spiral wire, and the glass on which it impinged became quickly covered with a thick dark coating. All the following lines were visible at the positive terminal:—

5607, 5546, 5372, 5043, 4386, 4245, 4020.

Silver.—With either $AgNO_3$ or $AgCl$ two strong green lines were seen at 5464 and 5208, but the nitrate is rather inconvenient to use on account of its ready fusibility. The chloride gave a curious effect in a high vacuum. When the discharge was first passed, the white chloride shone with a bright light green phosphorescence; but under the influence of the discharge it immediately darkened, and as it darkened the phosphorescence faded rapidly away. By shaking the tube a fresh surface of white salt was exposed, thus renewing the phosphorescence, which again quickly faded, and in this way the effect could be repeated a number of times.

Mercury.—Using Hg_2Cl_2 , the negative terminal and the space around it shone with a strong green light, almost like a flame; but the salt volatilised very rapidly, and the condensation on the sides of the tube soon prevented observation.

A sub-nitrate was more convenient in use, and gave a similar result. On the negative plate were seen green flashes of light, and when the spiral wire was made negative the green glow was very intense. There was a good deal of continuous spectrum, and the green line 5460 was very strong. Two other lines were well seen—one 5790, the other probably 4358.

Thallium.—The sulphate was used and always gave very good results. The terminal was surrounded by green flashes of light, and the line 5349 was very sharp and distinct.

I failed completely with rubidium and potassium, although several attempts were made with various of their salts.

With aluminium oxide, Al_2O_3 , I could see in short flashes a sharp line spectrum, but could not keep it visible long enough to fix the position of the lines.

Phosphoric anhydride gave a similar result. A good spectrum could be seen, but only in short quick flashes.

Boric anhydride gave feeble results. I could just distinguish the green bands of the oxide, which were very faintly visible.

A number of compounds of other metals were tried without much success, although in several instances there were indications that a slightly more powerful discharge would have been more effectual.

The general conclusions arrived at are as follows:—

The metallic lines have their origin in very small flickering luminous points, which appear on the surface of the terminal, and are not seen in the negative glow surrounding the terminal, except in the case of very volatile metals. These luminous points seem to be minute portions of the material momentarily raised to a very high temperature.

The best results are obtained with the more volatile metals.

The nature of the acid or state of combination does not seem to be of primary importance. All the compounds of Li or Na, for instance, seem to answer equally well.

Increasing strength of discharge increases effect, and as a rough general rule, the point of maximum brilliancy appears to be near the pressure of least resistance, and this indicates that density of current has an important influence.

No special advantage was obtained by introducing condensers into the secondary circuit.

These spectra can only be obtained at the negative terminal.

It is true that in one or two instances metallic lines were observed at the positive terminals, but I am inclined to think, from the general results, that this was due to a reverse current, as my coil at certain pressures and with terminals of equal size will show two negative poles in the same tube, the discharge being evidently alternating.

When a tube is first made it is sometimes rather difficult to lodge a little of the salt on the terminal; but immediately the discharge passes the coating becomes strongly adherent, and continually increasing with use, and in several cases the tube became non-conducting, apparently because the coating of salt was too thick to permit discharge to pass.

The spectrum effect frequently faded while the terminal was under observation, although it was still thickly coated with salt.

Jerking the tube so as to cause a fresh layer of material to reach it usually restored the effect, and was often accompanied by an instantaneous increase of brilliancy in the gaseous glow in the body of the tube.

The phenomena of electrical evaporation, as recently described by Mr. Crookes in the case of metals, was very marked in some of the experiments with compounds. Bodies like As_2O_3 , P_2O_5 , and Hg_2Cl_2 immediately volatilised when the discharge was passed, and condensed again in thick coatings on the sides of the tube.

The main object of my work was an endeavour to obtain information as to the nature of the actions which occur at the negative terminal during discharge, of which at present very little is definitely known. I am inclined to think that the spectral lines are only obtained when the discharge actually travels through a portion of salt in its passage from terminal to gas; and as the discharge through the salt must be of a disruptive character, the action is analogous to that which occurs in ordinary spark spectra in air. The effect of the spark in air is to volatilise and destroy the portions of salt in its path, and it therefore becomes interesting to inquire whether the vacuo discharge produces similar decomposition effects. It is evidently not sufficient that particles of salt should be raised to incandescence by the heat of the discharge; the metal must be actually in a state of vapour before sharp, bright lines can be obtained.

I have at present scarcely touched this part of the work, but the coatings on the terminals often became blackened and discoloured, and dark coatings on the glass were frequently met with. In the case of fairly stable salts I have been unable to detect the slightest trace of a rise of pressure in the tube, such as might be attributed to decomposition. The following experiment, however, seems to indicate that such an effect may occur to a slight extent:—A tube containing thallium sulphate, which had been in use during six months, was opened. The negative terminal was partly covered with a deep black powdery substance, the other terminal being nearly quite clean. The terminal was well washed, and then placed in water, which was slightly acidulated by means of a glass rod dipped in H_2SO_4 . The black coating immediately began to dissolve, accompanied by evolution of gas. When it had all disappeared the gas bubbles ceased also, and the solution gave the reactions of thallium; but the amount of black powder obtained was very small, especially in relation to the number of times tube had been used. I hope to experiment further in this direction.

Countess Street, Leicester.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 5).

If a loss of precipitate is not an object we may have recourse to the method of filtration recommended by Streng by means of narrow slips of paper. The port object with the drop which is to be filtered is laid upon a small board having a slope of about 1:20; a second is pushed up to the margin of the board so that the vertical distance of the two from each other is about 5 m.m. They are then connected by means of a slip of filter-paper of the shape of a Y, the arms of which are moistened so as to adhere to the upper glass, and the liquid to be filtered is brought into contact with the paper. The dimensions proposed by Streng, 2 m.m. in breadth, and 25 m.m. in length, may be reduced to 1.5 m.m. and 10 m.m. The quantity of liquid which is retained in and below the slip of paper amounts then to 5 m.grms. The precipitate does not fare so well, as much of it—if washing is necessary the greater part—soaks into the paper. This loss is diminished if an approximate separation can be effected by means of a wire as described above.

There remains, undeniably, room for improvements which will be very welcome if we do not lose what is good in our quest for something better. I have kept in view the small bulk of the apparatus, and the consequent possibility of working with it in all places, and at the same time the economy of time by avoiding unnecessary preparations. It must not be thought that especial genius is needed in order to work expeditiously and well with the simple means above described. Correct observation and independent thought are certainly needed and the operator must learn to work with little apparatus. All this applies, however, just as well to blowpipe analysis. If a fair attempt is made I am convinced that an experienced analyst who has made occasional use of the micro-scope will encounter no more serious difficulty with micro-chemical analysis than he once did with the blow-pipe.

Reactions.

I.—Potassium.

1. With platinum chloride. Lemon-yellow sharply developed octahedra of K_2PtCl_6 , refracting light strongly, sometimes assuming a hexagonal structure by flattening and combination with $\infty O \infty$. Size 10 to 50 micro. If rapidly deposited sometimes combined in threes and fours in the shape of a clover leaf or of a cross. Solubility 1:100. Limit of the reaction 0.0005 m.grm. K.

Use a strong solution of platinum chloride, which when drying up must not deposit octahedral crystals. A drop of this liquid of about 0.2 m.grm. is placed on the specimen drop, which should be neutral or faintly acid. In dilute solutions the yellow octahedra only form after a few minutes along the margin. An excellent reaction, if the presence of caesium, rubidium, and ammonium is excluded. An excess of strong acids, especially of sulphuric acid, reduces the sensitiveness of the reaction, but may be counteracted by an addition of sodium or magnesium acetate.

2. With phosphomolybdic acid. Minute crystals very similar to those described under 1; combinations of O with ∞O mostly globular, refracting light strongly, principally accumulated at the margin of the drop. Limit of the reaction about 0.0003 m.grm. K.

In using phosphomolybdic acid it must be noted that its solution on evaporation yields fine yellow octahedra, even if no alkali is present. The octahedra of the pure acid are sharply developed with straight edges, measuring 30–60 micro., whilst those of the potassium compound are rounded and about three times smaller. The reagent must be added freely; the sample drop is acidified

with hydrochloric or nitric acid, and a large drop of the reagent is added. It is useful for strongly acid solutions, but it must be used with caution, as besides potassium it precipitates caesium, rubidium, ammonium, and lithium.

3. With bismuth sulphate. Colourless hexagonal discs which are slowly developed to stellar, rhombohedral structures ($R-R'OR$ of 30–60 micro.), limit of the reaction 0.0002 m.grm. K.

Basic bismuth nitrate may be used, dissolved in nitric acid with the addition of a little sulphuric acid. The solution to be tested must first be concentrated. Nitric acid delays the reaction, but does not prevent it except in very large excess. Ammonium behaves like potassium with bismuth sulphate. Sodium is also precipitated, but in a quite different form.

4. With silicofluoric acid. Very small cubes with faint outline 10–20 micro.

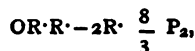
This reaction proposed by Boricky is not recommended on account of the smallness and paleness of the crystals, but it sometimes makes its appearance unintentionally during micro-chemical work.

II.—Sodium.

1. With uranylacetate (Streng). Pale yellow sharply developed tetrachloride of about 50 micro. Limit of the reaction 0.0008 m.grm. Na.

As a reagent we use a solution of uranylacetate in acetic acid. The sample liquid is to be strongly concentrated as the reaction is very faint at a dilution of 50. Strong acids should be expelled by evaporation, ammonium acetate being used only in cases of necessity, as an excess of ammonium salts interferes with the reaction. Streng adds that platinum chloride also interferes, which must be remembered with reference to potassium.

2. With uranylacetate and magnesium acetate (Streng). Rhombohedral crystals almost colourless; chiefly



according to the position and the predominance of tetrahedral, dodekahedral, rhombic, or hexagonal structure. Size up to 120 micro. Limit of the reaction 0.0004 m.grm. Na.

This reaction is produced under the same conditions as 1, if along with sodium metals of the magnesium group are present in excess.

3. With silicofluoric acid (Boricky). Hexagonal discs and short columns of the combination $\alpha P \cdot P$, measuring as much as 70 micro. From less dilute solutions there are thrown down elegant, six-leaved rosettes, of 80–120 micro. in size. Solubility 1:150. Limit at 0.00016 m.grm. Na.

Instead of silicofluoric acid may be used ammonium-fluosilicate if a granule is placed in the moderately acid sample. More massive crystals of sodium fluosilicate have a faint rose colour. Platinum chloride does not interfere. In highly diluted solutions the reaction appears only as evaporation proceeds.

4. Bismuth sulphate. Colourless hexagonal rods 20–80 micro. Limit of the reaction 0.0004 m.grm. Na.

Compare potassium No. 4. The reaction is serviceable for the simultaneous detection of potassium and sodium. To this end a solution of bismuth sulphate in dilute nitric acid is spread out in a layer of 0.3 m.m. in depth, and the sample in question is placed in the middle of the extended drop either as a solid or as a thick paste (sulphate). A short heating to 50–60° accelerates the precipitation of the sodium double salt which collects round the specimen. The discs of the potassium double salt appear later and diffuse themselves over the whole preparation.

Haushofer's test, potassium pyroantimoniate, did not give good results. The reaction was tedious and the crystals not well defined.

* Zeit. Anal. Chemis.

(To be continued).

THE SEVENTH INTERNATIONAL
CONGRESS OF HYGIENE AND DEMOGRAPHY.

NEXT month will witness a gathering which promises to be the leading scientific event of the season, and which will, we hope, leave its mark behind in the shape of permanent results. Looking at the papers already announced, we may venture to doubt whether they can receive due discussion in the time allotted. We must hope, to this end, that the readers of papers and other speakers will not indulge in self-advertisement, such as is often introduced on such occasions; and that they will, above all things, eschew the introduction of political considerations, for which two, at least, of the sections might supply temptation.

Our attention is naturally drawn chiefly to Section V., "Chemistry and Physics in Relation to Public Health." This section will hear and consider the following papers:—On Tuesday, August 11, a memoir on "Smoke and its Effects," by Dr. W. J. Russell, followed by a paper on "The Air of Large Towns, and Methods for its Analysis," by the Manchester Field Naturalists' Society, and a paper on the "Means at our Disposal for Preventing the Emission of Smoke from Factories and Dwelling-Houses," by Mr. A. E. Fletcher, H.M. Chief Inspector of Alkali Works, &c. Dr. C. Merdon Williams will take part in the discussion with regard to "fog from a hygienic point of view."

On Wednesday, August 12, there will be read papers on that much-disputed subject the "Treatment of London Sewage," by Dr. Dupré, F.R.S.; "Outline of the Various Chemical Processes for Purifying Sewage," by Dr. J. C. Thresh; "The Duties of a Locality to Secure the Nitrogen of its Sewage for the Benefit of the Nation," by Dr. A. Carpenter. It need scarcely be said that if the utilisation of such nitrogen is proved to be a duty, all those processes which aim at carrying sewage or sewage precipitates into the sea, and no less all those processes in which its constituents are converted into cements or otherwise destroyed as such, are at once condemned. Dr. A. Carpenter further contributes a paper on the power of soil and vegetation combined to destroy disease germs, and to prevent the possibility of a spread of enteric disease in consequence of sewage farms.

Herr Margraf, of Berlin, promises a paper, though he may possibly be unable to be present and take part in the discussion.

On Thursday, August 13, Prof. Dr. Lehmann, of Wurzburg, will bring forward a paper on "The Hygienic Importance of Copper," a subject as yet far from having been fully elucidated. There follow two other papers on subjects of great importance bearing upon public water-supply: "The Importance to be Attached to Magnesia in Drinking-Waters," by Prof. P. F. Frankland, F.R.S., and "The Action of Water on Lead," by Dr. J. H. Garrell.

Next follows a paper on "The Antiseptic Treatment of Food," by Mr. O. Hehner, and one on "The Effects of the Respiration of Carbonic Acid on Man," by Dr. W. Marcet, F.R.S.

On Friday, August 14, will be read an "Introduction to Meteorological Subjects," by Lieut. Strachey, F.R.S., followed by papers on the "Influenza . . . (?) of London," by Sir A. Mitchell and Dr. Buchan, and "Hygienic Improvements in the Manufacture of Bread," by Mr. J. Goodfellow.

It is further expected that papers for this section will also be contributed by Prof. Liebreich, of Berlin, and Prof. Lunge, of Zürich.

We see with regret that much of the matter to be taken into consideration in Section VII.—Engineering in Relation to Hygiene—is in its character distinctly chemical and physical, such as the chemical and electrical treatment of sewage, the quality of potable water, its purification and the pollution of rivers—subjects which can only be discussed by chemists, and on which chemists alone are qualified to adjudicate.

THE PROGRESS OF CHEMICAL THEORY:
ITS HELPS AND HINDRANCES.*

By Dr. PERSIFOR FRAZER, Prof. of Chemistry.

(Continued from p. 18).

THE long chemical war against phlogiston had been fought and won, and the thought of experimenters was turning in a new direction which was to institute a new war lasting only a little less long than the last, but the difference between the two cases was that whereas the phlogistic theory hung like a pall over the whole science, obscuring during its continuance the entire field; in this case the question in dispute was as to the ultimate constituents of matter, and none of the many views entertained on these questions interfered with the classification and assimilation of the myriads of facts which experiment and research were eliciting. This war, therefore, while it will serve to illustrate that the most eminent chemists share with the rest of the world the weaknesses of our common humanity, did not materially retard the progress of the theory of chemistry.

Proust (1755—1826) announced the unchangeable proportions by weight in which substances combine together; and that if they combine in more than one proportion it is by leaps and not gradually, as the water of the ocean becomes little by little more charged with salts brought down to it by the rivers. This was a great and pregnant discovery which at once led the way to the new field of battle, but the strangest thing about this announcement is that it was vehemently attacked by Berthollet (like Proust, a native of France), in a proposition which a little later seemed nothing but a stupid blunder or obstinate opposition, and yet in Berthollet's contention lay a precious truth only recently recognised and placed in its proper place.

Briefly, the skirmish between these two men was this. Proust discovered that the relative proportion to each other by weight of carbonic acid and copper in carbonate of copper was constant; no matter in how great excess one or the other of these bodies was present, the weight of the carbonate of copper was the same, and the weight of each constituent in it was invariable. For instance, substituting the accurate weights which better methods and apparatus have enabled chemists to obtain for the inaccurate approximations then made, in 123.4 grms. of carbonate of copper (there were always 63.4 grms. of copper, and 60 grms. of carbonic acid). It made no difference whether these weights of the two elements respectively, or whether two or three times as much of one with the above weight of the other were made to combine; the result was always that 123.4 grms. of the compound were found, and the excess of either element remained uncombined.

With tin and iron there were two proportions by weight in which each of these elements combined with oxygen, but there were no insensible passages from one to the other. Thus there was a compound of oxygen and tin in which 119 weight-units of the latter combined with 16 of the former; and there was another in which 119 tin combined with 32 of oxygen, but there was none in which the 119 weight-units of tin combined with any number of weight-units of oxygen between sixteen and thirty-one.

Berthollet (1748—1822) maintained, on the contrary, that if different masses of two elements are brought together, there will be found in the compound more of that constituent which was in greater quantity before the union. On account of the high position which Berthollet held in the chemical world this view received respectful, though silent attention, for few of the masters of the science were won over by it; because Richter, Klaproth, Vauquelin, and Wenzel had placed the constancy of acid and base in a compound of the two beyond all question.

* Introduction to the Chemical Lecture Course at the Franklin Institute, November 10, 1890.

Proust, however, took up the gauntlet and followed each separate publication of Berthollet by a refutation based upon careful experiment. This lasted for eight years, or from 1799 to 1807, and was settled apparently for ever when Proust, by repeating some of Berthollet's own experiments on the successive stages of oxidation showed that his opponent had mistaken a percentage of water for a percentage of oxygen.

But Berthollet's main idea that the mass and the affinity were inseparable factors in the formation of a compound, after having been crushed to earth, was to rise again in more recent times by the labours of his countryment of almost similar name, Berthelot and St. Gilles, and by Guldberg and Waage; but they showed, not that the proportion by weight of the compound, but that the rapidity of the reaction was affected by the masses of the constituents.

This dispute and the rise and fall of a theory was only a slight skirmish, which was preliminary to the general engagement. It had an admirable effect on the science, widened men's views, proved that the weapon of the future was to be a carefully conducted experiment; and without doubt ripened the next great discovery which was then about to be announced.

John Dalton (1766—1844) was led to the happy thought of taking the data of the weights which Proust had announced as those in which tin, iron, oxygen, &c., combined, and reducing them to their simplest proportions. Proust had found that some arbitrary number of grms. of tin (say, for example, 119), combined either with 16 or with 32 grms. of oxygen, and with no other weights. Dalton showed that the weights of oxygen in these two compounds were to each other as 1 to 2.

In the same way the different weights of sulphur which entered into combination with a given weight of iron were to each other as 1 to 2. And he found that this held for all cases where two constituents combined with each other in more than one proportion.

Thus, if the amount of hydrogen in olefiant gas or ethylene and marsh gas or methane are compared, they are to each other as 1 to 2. By numerous examinations of this kind, in all of which he found this simple relation, he was led to formulate his atomic theory, some of the more important propositions of which may be thus condensed. (1) Every element consists of similar atoms of fixed weight; (2) Chemical combinations are made by the union of the atoms in the simplest proportions. The atomic weight of a compound is equal to the sum of the atomic weights of its constituents. He supposed all the atoms to be spherical and to be surrounded by heat spheres (1).

It should be mentioned in passing that Higgins had said in 1789 that chemical smallest particles were united to form compounds in simplest proportions, but as he never adduced any proof of this, the merit of the discovery belongs to Dalton by the law of possession already alluded to before, viz., that in natural science not only must a truth be announced, but some reason for it must be given.

The immediate result of his postulates was that Dalton set out to establish a scale of atomic weights for the elements. Among minor postulates of his which have not lived till our day, but which were natural enough at a time when there were no means of obtaining certainty as to the questions of the number of atoms entering into combination, &c., was this, that if only one proportion by weight of a combination between two elements were known, it must be supposed that the number of atoms entering into this combination was one from each element. If two were known, then that in which the least weight of one combined with the least weight of the other must be considered 1 to 1; when with double this weight of the other the proportion must be 1 to 2, &c. In Dalton's time only one combination between oxygen and hydrogen was known, viz., water, and he assumed this to be composed of one atom of H to one atom of O. As H was

and is yet the lightest element known, he assumed its weight as one. By the imperfect methods then available, he determined the weight of O which combined with it to form water as 6.5 (in reality it is 7.98 if H=1).

Ammonia, which was the only compound of H and N known to him, and in which he also assumed one atom of each element, gave him the number 5 for the atomic weight of N. By accurate methods it should be 4.66. In the lowest compound of carbon and oxygen known, carbonous oxide, he found the atomic weight of carbon 5.4 calling oxygen 6.5 (the right figure is 6).

All his figures were wrong as we now believe because of his false assumption of the constitution of water (not to speak of his imperfect methods of analysis), yet the accuracy which he attained was surprising for his epoch and the invigorating effect on the science was as great as if all his numbers had been absolutely correct.

Humphry Davy (1778—1829), the great discoverer of the alkaline metals and earths, who first announced the elemental character of chlorine, and by his discovery of the halogen acids seemed to have overthrown Lavoisier's dictum regarding the invariable presence of O in all acids—Davy, the discoverer of the safety-lamp for miners, first announced his belief that chemical affinity and electricity were the same force. This idea was erected by Berzelius later into the splendid structure which he called the electro-chemical theory. Neither Davy nor Wollaston believed that Dalton's experiments had succeeded in establishing the nature and characters of atoms, but contented themselves with Wollaston's theory of "equivalents," without seeking to define how much matter entered into combination.

Their theory was that the atomic weights of Dalton were merely a series of arbitrary numbers, showing the respective quantities of different elements which were equivalent to each other in combining each with a third.

Wollaston's name of "equivalents" took root later after the apparent failure of Berzelius's theory to account for all the facts, and was the shibboleth of a long period of timidity and vacillation in chemical theory, which marked the reaction of thought when it was feared that the allurements of a beautiful system and the powerful influence of a great authority had drawn the representatives of the science away from sure ground. This period of intellectual cowardice was very tantalising and very confusing to those who pursued their studies during this period, but in the end it was an advantage to the science by letting the field lie fallow for a time, and making it thus the fitter to receive and develop the seed which finally was sown upon it.

In all cases where the development of a science has been rapid, it is found that the great minds are clustered together, and that the great discoveries occur in succession to supplement each other. It was stated that the discovery by Black originated pneumatic chemistry or the chemistry of the gases. In this field the discoveries of Cavendish, Priestley, and Scheele were made, but with the wider view given by Lavoisier to the science, the study of the gases was abandoned for the study of other solid and liquid compounds. But Gay-Lussac (1778—1850) devoted himself to pneumatic chemistry and accomplished in it what supplemented the work of Dalton, and prepared the way and assisted the researches of Berzelius.

In 1805, in conjunction with Alex. von Humboldt, Gay-Lussac established the fact that exactly two volumes of H combine with one volume of O to form water.

He showed the simple relations of the volumes of combining gases to each other and to their compound; he showed the effects of temperature on gases, and how it must be considered in connection with the Boyle-Mariotte law of pressure. His conclusion was that "The specific gravities of gases are proportional to their atomic weights, or are simple multiples of them."

Avogadro, an Italian chemist and physicist, attracted by the discoveries of Gay-Lussac, had, in 1811, deduced from the Boyle-Mariotte law that in equal volumes of two gases at the same pressure and temperature must be contained an equal number of physical particles. It was such a small step from these two beautiful generalisations to the conclusion that the smallest physical parts of elementary gases not being indissoluble must contain more than one atom, and that, therefore, here was proven the physical smallest parts, and the still smaller chemical smallest parts which are capable of entering into combination. But though Avogadro announced this conclusion in 1811, it was long years before it was taken up and embodied in the theory of the science. Gay-Lussac furthermore, by his work on iodine and cyanogen, laid the foundation of the "radicle," as his experiments on the action of chlorine on oils did the same for the "substitution theory." He is also the inventor of the method of volume analysis or titrimetry.

J. J. Berzelius (1779—1848) offers a life history such as few have been seen since the beginning of the world. It seemed as if the tangled skeins of nature's most intricate clues were straightened and cleared in his hand as if by magic; and the marvel of the magnificent work which he left as a monument to himself, his country, and the science to whose cause he was devoted, is that hardly a line of it needs to be erased, and the corrections of his constants are decimals representing the greater accuracy of apparatus at the present day.

In 1812 he created a new mineral system, in which the combination of the elements in multiple proportion was clearly indicated. His improved methods of analysis served to enable him in 1814 to show that also in organic chemistry this law prevailed. The atomic theory was made by him the guiding principle for the science. He explained the union of elements by the polarities peculiar to their atoms, and his electro-chemical theory founded upon this hypothesis brought him to the dualistic view of the combination of matter.

The reason why so little of his work needs to be changed is that he based everything upon investigation and experiment. The results which he achieved here will remain, no matter what theory may be the final outcome of further advance. He saw at once that Dalton's rule for determining the relative number of atoms in a compound was arbitrary and he pronounced it so. With the help of Gay-Lussac's discoveries of the gas volume relations and his own discovery of the oxygen law of relation between the acid and the base, he was enabled to draw correct conclusions as to at least 2000 bodies which he had personally analysed. He considered the unit volume represented by the atom, and he deduced the constitution of bodies by weight and by volume (as, for instance, water) as we understand them to-day. It is only fair to observe that Berzelius himself, in spite of his strong belief in the power of the volume theory to assist the investigator to a knowledge of the true atomic relations of a chemical element, recognised its limitations and rejected altogether the efforts to apply it to bodies which could not be studied in the gaseous state.

This is only just to bear in mind, because an onslaught against the splendid structure which his skilful hands had erected was caused by a mistaken notion as to Berzelius's real views of the atom volumes. This onslaught caused the paralysis of the faculty of speculation for many years among chemists, converting one of the most enchanting and exciting fields of discovery into the mechanical record of dry facts, which it was contrary to the fashion of the day to seek to unite under any common cause. Had Berzelius's teachings been properly understood and heeded there had been no occasion for this panic, and the last days of the grand old Pioneer would not have been embittered by the thought that the labour of his life, which was good work, was doomed to destruction.

The atom values which he had obtained in 1818 are given herewith.

	Berzelius.	Correct.
C.. .. .	12.12	12.0
O.. .. .	16.0	16
S.. .. .	32.3	32.06
Pb	416.0	206.95
Hg	406.0	200.00
Cu	129.0	63.4
Fe	109.1	56.0
Na	93.5	23.05
Ka	157.6	39.11
Ag	433.7	107.92

The reason that the values he obtained for the metals were so much higher than ours now, was that he then doubted the occurrence of other oxides than MO , MO_2 , MO_3 , &c., M standing for the metal. Instead of FeO , Fe_2O_3 , he wrote these compounds FeO_2 , FeO_3 , and consequently his percentage of iron was doubled. For similar reasons the metals K and Na received four times their normal weight, since he regarded the compound, which we know now as K_2O_4 , as KO_3 . Some years later he modified this position, admitting the existence of M_2O_3 , and his table then conforms nearly to the present. In his further classic work of determining the atom weights, he was assisted by the beautiful discovery of Dulong and Petit in 1819, that the atoms of all elements have the same capacity for heat, or that the product of the specific heat into the atomic weight gives a constant quantity.

Mitscherlich, a student of Berzelius, discovered that compounds of different elements which were similar in the number of atoms, the equivalent of water, &c., were isomorphic in crystallisation.

For example, in the phosphorus and arsenic salts only those which had like composition and like number of equivalents of water were isomorphic. Berzelius used both of these as guides, but showed a preference for the dictum of his former scholar. In his latter table of atomic weights of 1826, Berzelius corrected all but the alkali metals, which he still considered united to oxygen in the proportion of 1 to 1.

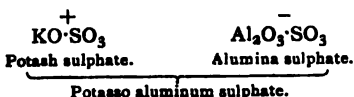
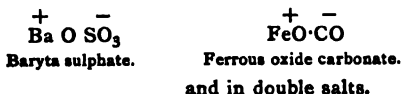
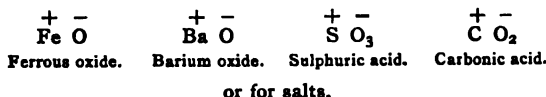
It will be recalled that Sir Humphry Davy and his school had pronounced chemical inseparable from electrical activity. He had shown that when a compound was decomposed by the electric current, and the separate constituents collected at the opposite poles (as, for example, sulphur and copper), these substances when rubbed or electrically excited showed opposite kinds of electricity: the substance at the negative pole showing positive, and that at the positive pole negative electricity. If the separate constituents (such, again, as sulphur and copper) were heated, the heat increased their electrical tension up to the point where they combined, and then all electrical activity ceased, the opposite kinds neutralising each other.

In conducting the current into the compound, its constituents received again electric polarity, and separated to the respective poles which attracted them.

Berzelius first stated his electro-chemical theory in 1812. His fundamental conception was that the atoms of bodies are electric, and therefore have at least two poles which generally are different in strength, and following this difference the elements which these atoms compose are electro-positive or electro-negative. This predominance of one kind of electricity extended to compounds, although necessarily more feeble in these. Compounds, according to this view, are the results of the attraction of the unlike poles of the atoms; and if in the compound there is a preponderance of one kind of electricity, this is because the atoms having this kind were more strongly polar than those having the other. Oxygen, as the most electro-negative of all bodies, was his criterion of the characters of the elements with which it combined. If the compound containing the least oxygen was basic, then the body combining with oxygen was electro-positive. If the oxide were an acid, then the element was electro-negative.

On this plan he arranged a table of elements in the order of their polarity. Of course it followed that any body in this table was electro-positive to all the elements on one side of it, and electro-negative to all those on the other.

His dualistic scheme followed as a matter of necessity, the two parts (whether the two elements or acid and base) having opposite polarities. Thus:—



Berzelius carried his dualism and his electro-chemical theory into organic chemistry. In 1813 he had discovered a simple relation between the elements composing the organic acid and the oxygen of the base, and had proved the combination in multiple proportions in organic chemistry, and it was he who recommended the study of organic bodies in their combinations with inorganic.

He supposed organic, like inorganic, bodies to be binary in constitution, but with compound radicles instead of simple elements. This was Lavoisier's idea. Gay-Lussac had characterised alcohol as consisting of ethylene and water; sugar as carbon and water. Döbereiner called oxalic acid a compound of carbonic acid and carbonic oxide. Berzelius opposed this conception as inconsistent with his electro-chemical theory. He could not acknowledge the existence of oxygen radicles. Yet the probability of such radicles was rendered strong by the discovery of organic bodies containing the same numbers of the same elements, yet exhibiting very different properties. This could only be explained by supposing that the proximate constituents were different.

Wöhler, Liebig, and Berzelius, after much hesitation, accepted the fact above referred to, and the latter designated the phenomenon as one of isomerism. Liebig and Wöhler had shown that a constituent of the oil of bitter almonds remained unchanged throughout a number of reactions, and this compound, of which the composition was $\text{C}_{14}\text{H}_{10}\text{O}_2$, they called benzoyl. (It is now called dibenzoyl or benzil).

At first Berzelius was disposed to accept this as an organic compound radicle, but reflecting that it must play the electro-positive rôle, although containing oxygen, he finally rejected this hypothesis, which he deemed inconsistent with his electro-chemical and dualistic theory; and he was led to the assumption of arbitrary radicles containing no oxygen, of which the formulæ, when written together, completely obscured the intimate relationships which existed between classes of salts. This was Berzelius's first fault, not so much due to his vanity as to the feeling which was well founded that the scheme he had with such infinite pains established was right; that it was being destroyed on theoretical grounds which, although he could not then satisfactorily answer them, with the instinct of a great genius he felt to be wrong. But his attempts to evade the conclusions only led him into self-contradictions which, when exposed, produced the same effect upon the chemical mind that the reported insolvency of a great banking house produces on the financial world. The failure of a Berzelius shut up the current coin of theorising the world over.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, July 6, 1891.

SIR JAMES CRICHTON-BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following gentlemen were elected Members of the Royal Institution:—Messrs. Henry Claudius Ash, Henry T. C. Knox, and John George Mair-Rumley.

The special thanks of the Members were returned to Miss Jane Barnard, Dr. J. H. Gladstone, the Rev. A. R. Abbott, Mr. T. F. Deacon, Mr. A. Blaikley, and others, for the loan of the valuable and interesting collection of Faraday Memorials shown in the Library on the occasion of the two Lectures on June 17th and 26th given in commemoration of the Faraday Centenary.

The special thanks of the Members were returned to Sir Frederick Abel, K.C.B., for his valuable present of an Oertling balance, and to Mr. Ludwig Mond for his donation of £100 towards expenses connected with the Faraday Centenary Commemoration.

The presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

NOTICES OF BOOKS.

Water Analysis: A Practical Treatise on the Examination of Potable Water. By J. ALFRED WANKLYN and ERNEST THEOPHON CHAPMAN. Eighth Edition. By J. ALFRED WANKLYN, M.R.C.S. London: Kegan Paul, Trench, Trübner, and Co., Limited. Small 8vo.

THIS manual has increased in size in its successive editions. The third edition, which appeared in 1874, numbered only 140 pp., whilst it now extends to 213 pp. But notwithstanding this enlargement the essential portion remains unaltered. The novel features of this edition are a chapter on specific gravity of drinking waters in connection with its purity or impurity. The author considers that "in extreme cases of well-contamination it might be desirable to take the specific gravity of the first small distillate yielded by a large quantity of the water." He very justly points out that this determination furnishes a check to the analysis. In these days it is difficult to say *à priori* what impurities may not be present in supposed potable waters, not to speak of river water and sewage. Mr. Wanklyn states that he in one case demonstrated the presence of benzol in a well water.

As a general rule he finds that the number of grains per gallon of total solids and of free carbonic acid approximately equals the number of centigrammes in excess of 1 kilo., which a litre of the water weighs. This seems to us a very useful result.

We find it stated that in many natural waters there is more carbonic acid in one state or other than "any other foreign material" taken singly. A considerable charge of carbonic acid in a natural water is laid down as a sign that the water has come from a considerable depth.

Mr. Wanklyn calls attention to the changes which waters undergo if kept for some time prior to analysis. The "free" ammonia decreases, and the "albuminoid" ammonia increases. Hence the interval between sampling and analysis becomes an important datum if different waters are to be compared.

The author's objection to magnesian salts in a water supply is perfectly justified.

A useful feature in this edition is the full account of

the "moist combustion process." As the patent for this process has expired, we hope that it will be widely tried and judged upon its merits.

On the value of the Wanklyn-Chapman process we shall not here make any remarks. We have expressed our opinion by occasion of the previous editions, and will now merely say that as the process has had twenty years' trial in nearly all civilised countries, it would have been abandoned before the present date if its results were unsatisfactory.

Piesse's Art of Perfumery and the Methods of Obtaining the Odours of Plants, the Growth and General Flower Farm System of Raising Fragrant Herbs. With Instructions for the Manufacture of Perfumes for the Handkerchief, Scented Powders, Odorous Vinegars and Salts, Snuff, Dentrifices, Cosmetics, Perfumed Soaps, &c. Edited by CHARLES H. PIESSE, F.I.C., M.R.C.S., &c. Fifth Edition. Published by Piesse and Lubin, 2, New Bond Street, London.

THIS work is something very much more than a treatise on the extraction and combination of perfumes. The author, in addition, treats his subject from the æsthetic and the biological point of view, and urges the development of the cultivation of the odoriferous plants in India and the colonies. He remarks in his preface that, "Of the five senses that of smelling is the least valued, and, as a consequence, it is the least tutored." This is unfortunately true. Yet as a means of scientific research smell comes second to sight alone, the place of hearing, except as a means of intercourse with our own species, being very low. In delicacy scent has been proved to exceed sight, even when the latter is aided by the spectro-scope. Scent impressions, too, are so permanent that an odour once experienced and not met with again for half a lifetime is at once identified on its recurrence.

Mr. Piesse thinks he is justified in saying that "England now produces the finest perfumery in the world." Yet, as he shows, very much more might be done in this direction if the resources of India, Australia, South Africa, and the Antilles were duly brought into play. We are too apt to undervalue any manufacture unless, like the iron, cotton, or woollen trades, it gives scope for the investment of millions of capital and the employ of thousands of hands.

Some of our industrial rivals have kept in mind the old Scottish proverb, that "Many a pickle makes a mickle."

In the history of the art of perfumery, Mr. Piesse falls into one error. He writes:—"After the Romans had conquered Egypt, India, and Arabia." It is certain that they never conquered India and that their jurisdiction over Arabia never extended to those parts most likely to yield odours.

As regards the production and diffusion of odours, the author concludes that here, as in the cases of colours, sounds, and heat impressions, vibrations are the active agents. In a long quotation from the late Dr. Septimus Piesse, it is contended that the action of odours depends on the "force of volatility." He has even drawn up a table of "the degrees of volatility of odours, which indicates pretty nearly their relative strength." He points out that the essences obtained from flowers by distillation are not identical with the perfume exhaled by the living flower. He suggests that in the former case we may have to do with a hydrate of the original odoriferous matter.

He holds that there is an octave of colours like the octave of sounds in music. He asserts, with perfect truth, that there is a harmony and a discord of smells. Anyone who has met a ladies' school taking a "constitutional" will often have been unpleasantly struck with the discords given off when several successive damsels have been scented with odours which clash. The impression is as unpleasant as when we see scarlet and magenta grouped together in the same costume.

We find mention of two conditions of the olfactory organs in man mutually opposite, though both abnormal. Anosmia, a more or less complete deadness to scents—we want a word corresponding to deaf and blind—is far from uncommon. Hyperosmia is present in its highest degree in male moths of the genera *Saturnia*, &c., which can recognise the presence of a female of their species at distances exceeding a mile, though woods, houses, fences, and eminences may intervene.

The emission of odours by flowers is in many cases periodically intermittent. According to Warren, aromatic orchids become scentless half an hour after pollen has been applied. The night-blooming *Cereus* gives out jets of odour every half-hour. Odours are preferentially connected with certain colours. White flowers are the sweetest, whilst orange and brown flowers are apt to have disagreeable odours, the final cause of which is still a riddle.

It is a remarkable circumstance that offensive smells, where they occur, pervade the entire plant, as in the elder, the rue, wild garlic, &c. In sweet-smelling plants the fragrance is, with few exceptions, confined to the flower.

The animal kingdom is far richer in nauseous odours than in perfumes, as a visit to the Zoological Gardens may convince the sceptic. To the perfumer the animal world yields merely ambergris, castor, civet, musk, obtained from the musk-rat of Canada and the musk-deer of Central Asia. The quantity obtainable from the musk-beetle (*Aromia Moschata*) is far too small to render its collection remunerative.

As regards the practical information with which the bulk of the work is filled, it would not be fair to the owner to make extracts. We will merely say that it bears the stamp of a practical man, as distinguished from the compiler. Whoever wishes to undertake either the theoretical study of perfumes or their practical manufacture will find here most valuable indications.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxii., No. 26, June 29, 1891.

On the Persulphates.—M. Berthelot.—The author publishes his observations as they have been independently reproduced in Germany by Herr Moritz Traube, and put forward in support of a singular theory on a supposed neutral "sulphurylholoxide." The composition of barium persulphate, S_2O_8Ba , may be regarded as absolutely determined. This salt is soluble and neutral like barium permanganate, and may be separated by filtration from the accompanying barium sulphate. The persulphate is slowly decomposed in the cold into insoluble barium sulphate which is precipitated, oxygen which escapes, and sulphuric acid which remains free. There is no proof of the existence of a pretended neutral anhydrous compound such as the imaginary holoxide, SO_4 .

Action of Sodium Alcohols upon Camphor. New Method of Preparing the Alcoylcamphors.—M. A. Haller.—The author has studied the action of sodium ethylate, propylate, isobutylate, and amylate upon camphor, of sodium benzylate upon dextro-camphor, the properties of dextrobenzyl camphor obtained by means of sodium camphor and benzyl chloride, of dextrobenzyl camphor prepared by reduction, benzylcamphoroxime, lævobenzylicamphor, and dextro- and lævobenzyborneol.

On the Oxidation of Azo-compounds.—Charles Lauth.—The author finds that, in a general manner, on

submitting the azo-compounds to the action of various oxidising agents in the cold, the azo-group is split up, yielding, on the one hand, a diazo-compound, and on the other bodies of the quinonic series. Both alkaline and acid oxidising agents have been tried. Both give analogous results, but as the former promote the decomposition of the diazo-bodies they ought to be rejected. He adopts by preference lead binoxide in preference to sulphuric acid.

Moniteur Scientifique, Queneville.
Series 4, Vol. iv., Part 2, No. 584.

Production of Cyanogen Compounds by Means of Atmospheric Nitrogen.—A. Breneman. — The author discusses the various conditions which have an influence upon the fixation of atmospheric nitrogen.

A Novel Method of Preparing Alkaline Nitrites.—G. A. Le Roy. — The author, after enumerating a number of methods already known (including a process of reduction by means of microbia discovered by Gayon and Petit) describes his own procedure. He causes 1 mol. BaS to react upon 4 mols. NaNO_3 , obtaining thus the soluble nitrite and the insoluble barium sulphate. He mixes the two substances finely powdered, projects them by small portions into a cast-iron bowl previously heated to dull redness, and stirs the fused mass continually. The reaction takes place with effervescence; the mass is taken up in water, which dissolves the nitrite; the liquid is decanted, filtered, and concentrated to $35^\circ\text{--}45^\circ\text{B}$. The barium sulphide employed must be free from carbon.

Rapid Process for the Preparation on the Large Scale of Silicon and Aluminium Chlorides and other Chlorides.—H. N. Warren. — From the *Chemical News* and the *Chemiker Zeitung*.

Sulphuretted Colouring Matters of the Primuline Group.—E. Trautmann. — This paper does not admit of useful abstraction.

Summary of Some Researches on Colouring Matters.—F. Reverdin. — This paper includes a notice of Flimms' synthesis of indigo by means of monobromoacetanilide and of Seidel's triphenyldioxazine.

On Tannins.—Etti. — The author considers the extraction of tannins, the preparation of the phenylhydrazones of tannin; the production of its oxime and the constitutional formula of the acetonide anhydride of gallic acid.

Distinction between Tannins Extracted with Alcohol and Those Extracted with Water.—Adrian. — From the *Bulletin de la Société Chimique*.

Use of Creosotic Acid in Tanning.—J. Hauff. — From the *Journal of the Soc. Chemical Industry*.

On Benzoyl Tannin.—Dr. Carl Böttinger. — If a dilute cold aqueous solution of tannin is treated with 5 c.c. of strong soda-lye, with the addition of benzoyl chloride, there is a reaction on stirring. The liquid at first turbid, becomes then dark, then red, and finally clear. A viscous matter is precipitated, which solidifies into small white globules. This mixture, on treatment with ether, gives a pasty mass. When taken up in water the substance hardens and yields; when dried, a light yellow powder, insoluble in water, and boiling alcohol. It is soluble in aniline, dimethylaniline, phenylhydrazine, and slowly in hot soda-lye. The compound required is separated and purified by a tedious process.

MISCELLANEOUS.

The Durham College of Science, Newcastle-upon-Tyne.—Dr. Wm. C. Mackenzie has been appointed lecturer in Agricultural Chemistry in this College. Dr. Mackenzie was for four years assistant to Mr. Falconer King, of Edinburgh, in which capacity he gained

great experience as an agricultural chemist in the analyses of manures, feeding-stuffs, &c. For three sessions he studied chemistry under Professor Crum-Brown at Edinburgh, obtaining the degree of B.Sc. and a number of medals and prizes. After this he studied a year under Professor Fittig, at Strassburg, and then obtained the degree of D.Sc. at Edinburgh, together with the Vaus Dunlop Scholarship of the value of £100 per annum for three years. At present he is working at agricultural chemistry as assistant to Professor Dr. Märcker, at Halle. Dr. Mackenzie will commence his duties in the College in September next.

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THE CHEMICAL NEWS.

VOL. LXIV., No. 1632.

ON THE NATURE OF SOLUTION.

(No. II.)

By J. ALFRED WANKLYN and WILLIAM JOHNSTONE.

It has been shown that in the instance of cane-sugar there is neither expansion nor contraction when solution takes place, the volume of the solution of sugar being exactly equal to the volume of the sugar and the volume of the water forming the solution.

Starting with pure water, 100 c.c. of which weighs 100 grms., we may regard solutions of sugar as generated by the entrance of successive grms. of sugar into the 100 c.c., and the displacement of the corresponding quantity of water.

The increment of weight occasioned by the entrance of 1 grm. of sugar is given by the following formula:—

$$i_1 = 1 - \frac{1}{\text{sp. gr.}}$$

where i_1 equals the increment, and sp. gr. is the specific gravity of sugar.

It will be obvious that $\frac{1}{\text{sp. gr.}}$ is the weight of the water displaced by 1 grm. of sugar; and, as was shown in the former paper, the experimental result corresponded exactly with the theory. This may be conveniently symbolised by writing—

$$i = i_1,$$

where i equals the result of experiment, and is obtained by dividing the actual increment of gravity in a given instance by the number of grms. of sugar in the 100 c.c. of the solution of sugar.

It has already been shown that common salt behaves somewhat differently in the act of solution, and that in that case i is considerably greater than i_1 . This we look upon is due to the circumstance that something besides solution takes place when salt dissolves in water. Picturing to ourselves the course of events, we see the gramme of salt entering the 100 c.c., but, instead of an equal volume of water being displaced and overflowing out of the vessel, there is chemical combination between salt and water and condensation, or absorption of part of the water.

This absorption is the difference between the value i and the value i_1 , and $i - i_1$ = the weight of the water condensed or absorbed when one grm. of a substance enters into 100 c.c. of solution.

Continuing the investigation we have experimented upon nitrates and sulphates as follows:—

Nitrates.

i .	i_1 .	
0.696	0.553	NaNO ₃ .†
0.582	0.524	KNO ₃ .
0.639	0.470	Ca(NO ₃) ₂ .
0.755	0.566	Sr(NO ₃) ₂ .
0.782	0.686	Ba(NO ₃) ₂ .
0.783	0.756	AgNO ₃ .
0.892	0.773	Pb(NO ₃) ₂ .†

The only nitrate, so far as we have gone, which occasions little or no condensation of water on solution, is nitrate of silver. There is not much condensation in the case of the nitrate of potash, only 0.058 grm. of water being condensed by 1.000 grm. of that nitrate. The ratio is almost absolutely that of 18 : 303.3 or H₂O : 3KNO₃. The case of nitrate of soda is quite different—0.143 : 1.000 is the

ratio, or 2H₂O : 3NaNO₃. In the case of nitrate of strontia, the ratio is 0.189 to 1.000, being about—



Sulphates.

i .	i_1 .	
0.784	0.632	K ₂ OSO ₄ .
0.910	—	Na ₂ OSO ₄ .
0.974	—	FeOSO ₄ .
1.00	—	CuOSO ₄ .
0.89	—	MgOSO ₄ .

We defer our communications on these results until our next paper.

The Laboratory, 13, Fish Street Hill, E.C.
July 20, 1891.

MATTING THE SURFACE OF GLASS.

By NICHOLAUS S. NILSSON.

"WHITE ACID" is a name used by glass etchers to designate mixtures of hydrofluoric acid with various chemicals which are used for matting the surface of glass. The discovery of white acid is due to Berzelius, who, while engaged in his investigations on the properties of glass, made the discovery that fluoride of ammonium had the property of matting or opaquing glass. Since that time it has been found that other alkaline fluorides possessed the same power, and during the last few years this has been taken advantage of on a large scale for producing ornaments on glass of the greatest beauty. It is employed, principally, for producing ornamental figures on door lights, although it is used very extensively for decorating glass-ware for table use, and also for the various sorts of globes used on lamps and gas fixtures. Extremely fine effects may be obtained on mirrors, and the silvering may be placed on either the same or the opposite side from the etching.

During the last few years etching on glass has shown itself as a formidable rival to the sand-blast. The work generally being indistinguishable from that produced by the latter, except that acid is capable of producing effects of a much greater fineness and delicacy. The grinding is much more even, and therefore more easily cleaned.

In Germany, where the art has been carried to a much higher point of perfection than elsewhere, a number of formulæ for matt-etching are in use. Within a short time some of these have been published in various scientific journals, but they all belong to the category of what might be called slow acids, and are very unreliable and uncertain in their action, and possess very poor keeping qualities. They are made without the ammonia salt, and are dependent on soda and potash for their action, take a long time to work, and are too uncertain for practical use.

There is no doubt whatever but that the white acid, compounded with fluoride of ammonia, is the best. In using other white acids, spots and streaks often form in the glass, and these cannot always be removed by repeating the etching. With ammonia acids, however, any streaks which may appear, either from applying the acid unevenly or from imperfections in the glass, may be removed by repeated etchings. The following recipe is one which is used by several practical glass etchers, and is said to give good results. It is of German origin, and the only objection to it is that it is too complicated, which objection may also be raised to other recipes from the same source.

In a container of lead the following mixture is made:—

Distilled water	500 parts.
Fluoride of ammonium (strong) ..	500 "
Sulphate of ammonia	50 "
Sulphuric acid	100 "

This solution is ready for use within two hours, and may be tested by immersing a piece of clean glass, which should get a nice, fine, matt surface after five or six minutes.

In practical experience the writer has found that a simpler method of preparing the acid than the foregoing is capable of giving good results. Besides being cheaper, it is possible to recover the materials in it, should it for any reason get out of order.

A container of sufficient size is filled one-third full of ordinary commercial hydrofluoric acid. Carbonate of ammonia is then added. About equal parts by weight may be used. When effervescence has ceased, a small slip of clean glass is immersed in the mixture, and permitted to remain six or eight minutes. Upon withdrawing it is rinsed in clean water, wiped, and dried. If examination shows that it has become evenly translucent over its entire surface, the mixture is all right and may be used for regular work. If, however, it is deeply and irregularly etched, with some parts clear and some parts ground, the acid is in excess, and carbonate should be added. If, on the other hand, the glass seems to be only partially affected by the acid, and, while being slightly ground all over, is transparent, too great an amount of ammonia has been used, and acid must be added.

With a little experience it is possible to keep the balance between the alkali and the acid, so that good results can be obtained. All white acids are subject to change in their actions from day to day, but in none of the recipes the writer has used can it be so easily regulated as in the foregoing. Before trusting any important work to the action of white acid, the acid should be tested with a clean piece of glass, and, by following the hints given, the acid can be corrected to give the proper action.

In preparing glass for etching any of the ordinary resists may be used. The drawing may be either put on glass by means of a ruling pen dipped in asphaltum properly diluted; by means of a brush; or by means of the somewhat antiquated process of covering the entire plate with Brunswick black and scraping away the parts which it is desired to grind. The best method, however, is that in which tin-foil is used, a description of which must be deferred to some future time. The design can also be transferred or photographed on glass if desired.—*Scientific American*.

ATOMICITY CUBES.

By J. BRAIK MASON, F.C.S.

TEACHERS of chemistry have found it somewhat difficult to get young students to grasp the facts of atomicity. This constantly recurring stumbling-block in the path of the learner led me to devise a simple mechanical contrivance, which has been found a great help in the way of imparting a better comprehension of things pertaining to the atom. There is usually found no particular hardship in grasping the nature of the atom itself—an ultimate particle, and therefore incapable of further subdivision. What offers the real hindrance to progress is the varying binding powers possessed by the different atoms. How to get a definite grasp of valency forms the difficulty.

To suggest a concrete assumption of what may be assumed as taking place, I take a number of square blocks of wood, painted white or different colours (or covered with paper), and proceed to liken one of these to an atom, explaining, of course, that an atom is so exceedingly small as to be incapable of being seen—an atom of any definite substance, as hydrogen, or oxygen, or sulphur. But, except that it may represent one atom of substance, it has no other character of its own. It does not represent a monad, or a dyad, or any other valency.

To give the atom a distinct monatomic character, a small screw, with hooked head, is inserted in one side, and this now represents a monatomic element, as H or

Cl. Another similar hooked on then represents a molecule of H_2 or HCl . A dyad element, as oxygen, with its two bonds may be represented by a block with two screws, one opposite the other; and thus the molecule of water may be illustrated, the dyad bound to two monads. A block with three attachments for a triad, as P or Bi; and one with four hooks would represent a tetrad, as C or Si; and so on.

In this manner, by showing several examples of combination, taking representative compounds, I demonstrate what is generally admitted a difficult point, and succeed in producing in the minds of the youngest a conception of various atomicities that is readily grasped and accepted.

Laboratory, Y.M.C.A., Constitution Road, Dundee,
July, 1891.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 32)

III.—Lithium.

1. With ammonium carbonate. Needles and prisms resembling crystals of gypsum and forming like the latter on the margin of the drop. They are slowly dissolved by water. Limit of the reaction at 0.00036 m.grms. Li.

2. With ammonium fluoride. This reaction, recently proposed by Carnot for the quantitative separation of lithium, produces mainly small colourless cubes, 15–25 micro; immediately surrounding the ammonium fluoride there are rectangular dendrites up to 100 micro. The sensitiveness of the reaction is a little inferior to that of No. 1.

IV.—Cæsium.

1. With stannic chloride (Haushofer). Sharply developed, colourless octahedra of 30–40 micro, much less soluble in hydrochloric acid than the chlorostannates of potassium and rubidium. Limit of the reaction about 0.0016 m.grm. cæsium.

The liquid is evaporated to dryness and the residue dissolved in dilute hydrochloric acid before the stannic chloride is added. Salts of ammonia must be expelled by a strong heat after evaporation to dryness, as the ammonium chlorostannate is likewise very sparingly soluble in hydrochloric acid. Sometimes it is advantageous to convert the chlorostannate into the yellow iodo-chlorostannate by an addition of sodium iodide.

2. With ammonium silicomolybdate. Crystals like those of potassium phosphomolybdate, but much smaller, 2–6 micro. Limit of the reaction about 0.00025 m.grm. Cs.

As reagent there is used a saturated solution of ammonium silicomolybdate in water. It is not precipitated by salts of potassium, sodium, and lithium. Ammonium chloride precipitates rounded crystalline grains of 8–12 micro; rubidium chloride yields similar granules of 8–20 micro; thallium salts fall in still smaller granules than those of cæsium. The reaction succeeds best in solutions which contain a little free nitric acid.

Instead of silicomolybdate there may be used a saturated faintly acid solution of potassium platinum chloride or an acid solution of platinum chloride in 300 parts of water if evaporation is prevented. Concentrated solutions of cæsium are instantly precipitated in very fine crystals (3–5 micro.); rubidium falls afterwards in crystals three times larger.

V.—Rubidium.

1. With ammonium silicomolybdate. The crystals of rubidium silicomolybdate are distinguished from those of the cæsium compound just described merely by their

* *Zeit. Anal. Chemie*.

size. They measure 10—20 micro. The limit of the reaction lies at 0.007 m.grm. rubidium; the limit of instantaneous precipitation is at the 100 fold dilution of rubidium chloride, whilst caesium chloride is at once precipitated at a 300 fold dilution.

In order to detect rubidium in presence of caesium the latter must be precipitated by an excess of stannic chloride in a strongly acidulated solution. After five minutes the clear liquid is drawn off and a little more stannic chloride is added. If after waiting for five minutes there is no further formation of octahedra, it is evaporated, ammonia is added, and after further evaporation and strong heating it is extracted with water. The clear extract is concentrated by evaporation, and tested for rubidium with ammonium silicomolybdate. Check experiments showed that traces of caesium escape precipitation with stannic chloride.

2. The precipitation of rubidium with platinum chloride has been already mentioned when speaking of caesium.

Precipitation with tartaric acid or sodium bitartrate cannot be recommended, as much potassium falls along with the rubidium.

VI.—Thallium.

1. With hydrochloric acid. From highly dilute solutions there are precipitated cubes of 10—15 micro.; from concentrated solutions cruciform rosettes of 50—100 micro. They are white by reflected light, but nearly black by transmitted light. Solubility 1:400. Limit of the reaction about 0.00016 m.grm. Tl.

Thallous chloride is rather easily soluble in hot water. From such a solution isolated cubes are always obtained. Sulphuric and nitric acids have also a solvent effect, and reduce the sensitiveness of the reaction.

2. With iodides. The same forms as under No. 1, but smaller. The rosettes measure at the utmost 20 micro. They are deep yellow and almost opaque. Solubility 1:4500. Limit of the reaction about 0.00003 m.grm. Tl.

3. With platinum chloride. Yellow octahedra, larger than those of caesium-platinum chloride, which they otherwise much resemble. The reaction is exceedingly sensitive; its limit is about 0.000008 m.grm. Tl.

Phosphomolybdic acid gives very similar crystals. Alkalies convert the precipitate into thallous molybdate. (See Molybdenum).

VII.—Silver.

1. With chlorides and ammonia. Silver chloride dissolves in hot hydrochloric acid and crystallises from this solution in octahedra (Streng); it dissolves more readily in ammonia ((Haushofer), and crystallises on evaporation in cubes and combinations of ∞ 00 and O. The crystals are definite but small (10—20 micro.), and refract light strongly. Limit of the reaction about 0.0001 m.grm. Ag. Chromates, phosphates, and arseniates have no influence. Gold chloride and platinum chloride produce dendritic structures of 50—90 micro. Mercuric chloride and ammonium molybdate interfere, and stannic chloride prevents the crystallisation.

2. With potassium bichromate. From solutions which contain little free nitric acid, the chromate, Ag_2CrO_4 , separates out in large blood-red prismatic crystals, which may reach a length of 300, or even 2000, micro. The solution in ammonia does not yield good crystals. Large specimens may be much more readily obtained by repeatedly heating in the slightly acid mother-liquor. Limit of the reaction about 0.00015 m.grm. Ag.

VIII.—Magnesium.

1. With phosphor-salt and ammonia. Hemimorphous crystals of the rhombic system of 10—20 micro. From solutions containing more than 0.5 per cent Mg there are first deposited X-shaped skeletons and rudimentary crystals of the shape of letter-envelopes. Composition— $\text{Mg}_3\text{H}_4\text{N}_2\text{PO}_4 \cdot 6\text{H}_2\text{O}$. Solubility 1:15000. Limit of the reaction 0.0000012 m.grm. Mg.

To the specimen drop there is added sufficient ammonia

and ammonium chloride; it is moderately heated and the precipitation is then effected by means of a granule of phosphorus salt. Application of heat, as proposed by Streng, much facilitates the formation of perfect crystals. It must be remembered that mixed crystals may be formed with the isomorphous double phosphates of ammonium and iron, manganese, cobalt, and nickel. Iron and manganese may be removed by waiting a couple of minutes between the addition of the ammonia and the phosphate. (See also Cobalt and nickel). It must be remembered that the reaction sometimes fails if the quantity of ammonium chloride is insufficient.

IX.—Glucinum.

1. With potassium oxalate. Massive crystals of a double oxalate which refract light strongly, of the form of natural crystals of gypsum, also swallow-tailed twin crystals, and forms produced by the coalescence of twins. Strong polarisation. Extinction below 40° . Size 100—200 micro. Limit of the reaction about 0.00008 m.grm. Limit of immediate precipitation at the 600 fold dilution of crystalline glucinum sulphate.

A small addition of potassium oxalate precipitates merely concentrated solutions of glucinum sulphate. There are formed X-shaped dendrites of an easily soluble oxalate. A moderate excess precipitates the double salt which has been already described and which is much less soluble. A large excess gives aggregates of pale lenticular rhombic crystals. Ammonium oxalate precipitates badly and sodium oxalate not at all. Ammoniacal solutions are to be evaporated to dryness, and the residue must be re-dissolved in hydrochloric acid. The solution must be neutral, and the potassium oxalate in excess.

With uranyl acetate and sodium acetate glucinum behaves like magnesium. (See Sodium).

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1891.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, July 6th, 1891.

SIR,—We submit herewith the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined, the whole were found to be clear, bright, and efficiently filtered.

The water supplied to the Metropolis during the month of June, though not exhibiting that extreme degree of freedom from organic matter—present in small proportion

in potable waters generally—which characterised the supply for the previous month, maintained, however, the satisfactory character which the Metropolitan water has now presented continuously since the period immediately following on the breaking-up of the severe and exceedingly prolonged frost of last winter, the exceptional results afforded at that period being made a subject for comment in our report for the month of February.

During the past six months we have examined 1008 samples of the water distributed to the Metropolis by the companies drawing their supplies from the Thames and the Lea. The generally excellent quality of the water is shown in the abstract set forth in the following table of the results afforded by the Thames-derived supply during each of the consecutive six months respectively, the results afforded by the entire supply furnishing even yet lower figures.

	Ratio of brown to blue tint.	Oxygen re- quired for oxidation.	Organic carbon per 100,000	Organic carbon per 100,000
	Means.	Means.	Means.	Maxima.
January ..	—	0.044	0.142	0.165
February ..	—	0.081	0.263	0.489
March ..	14.1 : 20	0.049	0.146	0.209
April ..	13.9 : 20	0.055	0.155	0.190
May ..	9.6 : 20	0.042	0.136	0.150
June ..	14.4 : 20	0.060	0.153	0.181

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

NOTE ON THE CALIBRATION OF BURETTES.

By DOUGLAS CARNEGIE, M.A.

THE method of calibrating burettes given in the text-books is roughly as follows:—

The burette is filled with water, and successive portions—corresponding to 5 c.c. or so—are run out into dry beakers. From the weights of these successive portions a table of corrections can easily be deduced. This method, in the case of an ordinary 50 c.c. burette and with 5 c.c. tests, involves at least eleven weighings and ten level-readings.

The method of calibration I would suggest is, I believe, more accurate than the above, and involves no weighing whatever; for it is quite a matter of indifference to the chemist, whose measurements are all relative, whether he adopts as his unit the true cubic centimetre or an arbitrary one.

The principle of the method consists in causing a constant volume of liquid to slide in the burette (so that it may be made to assume any desired position therein), and then reading off its length in terms of the burette divisions.

In fig. 1 the burette, B, is attached by means of caoutchouc tubing, C, to a reservoir, R, which is filled with water, and which can easily be raised or lowered by sliding the clamp K along S. On the surface of the water in the burette there is a small column of carbon bisulphide, W, which obviously can be made to assume any desired position in the burette by either raising or lowering R, and then turning the stopcock, N, very gently.

In my first experiments I used mercury in place of water in R, and water instead of carbon bisulphide as a movable index. But this combination was unsatisfactory; I found it exceedingly difficult to read the level, I, both on account of the convexity of the mercury surface and also on account of the peculiarly disturbing light reflection from the bounding water-mercury surface.

The combination, water and CS₂, works admirably if the following precautions be taken:—

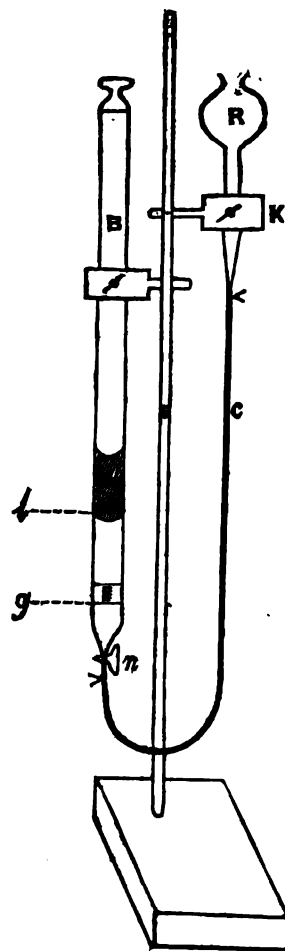


FIG. 1.

The burette must be *thoroughly cleaned* from grease and dust before calibration. The reservoir, R, is then filled with freshly distilled water, and matters are so arranged that the level of the water stands at *g*, the *lowest* graduation of the burette. A long thistle funnel is then inserted into the burette, and a small quantity (say

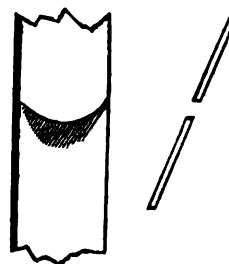


FIG. 2.

5 c.c.) of recently distilled CS₂ is poured gently on the surface of the water. Under these circumstances the CS₂, in spite of its higher specific gravity, floats on the water, and exhibits two easily localised concave menisci. It is well to shake the CS₂ up with distilled

water so as to thoroughly saturate it, and to tint it slightly with iodine before pouring it into the burette.

The method of procedure is obvious. I will merely add that, in altering the position of the CS_2 index, it is well to let it rise a little higher in the burette than the required graduation, and then lower it by careful manipulation of the stopcock, *n.* The burette should of course be kept stoppered as much as possible during the calibration.

I would also particularly emphasize the fact that the method works satisfactorily *only* when the calibration is effected as described—from below upwards.

The readings obtained can be used for calibration as described in detail in Bunsen's "Gasometry."

In order to avoid errors of parallax in reading off the levels of the CS_2 column, I silver a strip on the back of the burette. This mirror strip, which does away with all floats and similar devices for avoiding errors of parallax in the subsequent use of the burette, is easily made as follows:—The burette, having been thoroughly cleaned externally, is corked air-tight, and then inverted in a tall cylinder containing an alkaline silvering fluid.* After some time it is withdrawn, and allowed to become *thoroughly air-dried*. The silver can then be easily removed from the front and sides by scraping, followed by a final rubbing with a rag moistened with dilute nitric acid. The strip of silver backing the burette is then fixed by one or two coats of varnish.

In reading such a burette it will be found advantageous to look at the meniscus through a slit cut in a sheet of white glazed paper, held at an angle to the vertical as shown in fig. 2. The burette graduations are also rendered very much more distinct by rubbing the front of the burette first with a piece of flannel on which a paste of turpentine and mercuric iodide has been placed, and then with a dry cloth.

NOTES ON

CARBON IN "EXPERIMENTAL STANDARD."

By P. W. SHIMER.

My first results on the "Experimental Standard" distributed by Prof. J. W. Langley among the members of the American Committee on International Standards of Iron and Steel, were 1.055 per cent carbon in the sample marked "Ingot," and 1.052 carbon in the sample marked "Hammered." These results were obtained by use of double chloride of copper and ammonium solutions and combustion in a porcelain tube with the usual purifying apparatus, including anhydrous copper sulphate tube. These determinations were made before it was known that the double chloride usually contains carbonaceous matter. The copper solution was made as nearly neutral as possible before using.

After Dr. Dudley had shown that the results obtained by use of the double chloride of copper and ammonium could be varied by varying the method of making the double chloride, I endeavoured to determine the absolute total carbon by direct combustion of the steel in a current of oxygen. Owing to the length of time required to make a direct combustion in a porcelain tube (four to six hours) these efforts were not successful. The combustions were made on the "Ingot," reduced by grinding until part of the sample passed through a 35-mesh sieve. This fine material was then burned in oxygen in a porcelain tube. In some of the experiments the steel was intimately mixed with coarsely crushed Fe_2O_3 previously ignited to constant weight in oxygen. In other experiments CuO was used in place of Fe_2O_3 . In still other cases, a long copper boat, previously ignited to constant weight in oxygen, was used. The powdered steel was evenly and

thinly spread on the bottom of the boat, which the ignition had covered with a coating of CuO . The results of six combustions were—1.072, 1.058, 1.077, 1.065, 1.076, 1.072. These results were not worthy of confidence, because of the strain upon the constant weight of the potash bulbs by reason of the long combustion of four to six hours. Suspecting that the oxygen might contain a trace of carburetted gas not absorbed by KOH solution, I placed a second porcelain tube containing CuO directly above the combustion tube in the furnace. On making a combustion, the oxygen was first passed through the upper tube, then through KOH , then into CaCl_2 tube and combustion tube. In this way a good constant weight could be maintained for long combustions. By this arrangement a direct combustion, requiring five hours, gave 1.047 per cent carbon in the "Ingot."

If the double chloride of copper and ammonium contains carbonaceous matter it occurred to me that it might perhaps be removed by filtration of the solution through charcoal. For this purpose a glass tube, 27 inches long, was filled with crushed charcoal, and the copper solution was slowly filtered through it, being finally passed through ignited asbestos to remove minutely divided carbon in suspension. Samples of 3 grms. each of the "Ingot" were dissolved in 200 c.c. of the above filtered copper solution previously made acid by addition of 10 c.c. HCl , sp. gr. 1.12. The results were 1.036, 1.034.

The original copper solution, without filtration through charcoal, was then used in the same way. The result was 1.040. This difference is not large enough to have any decisive significance. But it will be worth while to try the effect of filtration through charcoal upon a more impure sample of the double chloride than mine happened to be.

I next tried the double chloride of copper and potassium as a solvent in the manner recommended by Mr. Blair. The results were 1.036, 1.038.

After the solution of the steel in the above five determinations, the carbon residues were filtered upon ignited asbestos (without use of suction) in Dr. Drown's wide-necked carbon funnels. (*Journ. of Anal. and Applied Chem.*, ii., 330.)

When the carbon was all in the funnel, the asbestos was liberally soaked with cold HCl , sp. gr. 1.12, and allowed to remain in this condition for a few minutes, in order that all chlorides might be rendered easily soluble. The carbon was then washed (without suction) with hot water, twenty to thirty times, until the filtrate showed no chlorine by silver nitrate. After drying at 90°C ., the carbons were transferred to the porcelain combustion tube, which contained nothing but the usual CuO . The apparatus was put together in the following order:—1. Oxygen tank; 2. Porcelain tube containing CuO , placed immediately above the combustion tube in the furnace; 3. KOH bulbs; 4. CaCl_2 tube; 5. Combustion tube containing CuO ; 6. A Liebig potash bulb, containing nothing but a drop of water in each of its five bulbs, and cooled by filter-paper kept wet by dipping in cold water; 7. CaCl_2 tube; 8. KOH bulbs, with the usual CaCl_2 tube attached; 9. A guard of CaCl_2 . After completing the above five combustions, the few drops of water were removed from the Liebig bulbs, and found to contain no chlorine when tested by silver nitrate. Evidently the method of washing the carbon residue (by liberal treatment with HCl and thorough washing without suction) has removed all chlorides, for any hydrochloric acid or chlorine escaping from the combustion tube would be condensed or absorbed in the cold and moist Liebig bulbs. I cannot help thinking that a too sparing use of HCl on the carbon residue, and a too rapid washing by suction, is responsible for much of the trouble with hydrochloric acid and chlorine. In order that wash-water may thoroughly dissolve impurities, it must be given time to act upon them. From the fact that the results obtained as detailed agree so closely with the results obtained in the admirable apparatus devised by Mr. Blair, I am

* Suitable fluids are described in Roscoe and Schorlemmer's "Treatise on Chemistry" vol. ii., part 1, p. 363

still further encouraged to believe that the HCl difficulty may perhaps be overcome at its source by washing in the manner described, and, as a further precaution, by the use of some simple condensing and absorbing arrangement, like the moistened Liebig bulbs. More experiments, however, be made to decide these points.—*Journal of Analytical and Applied Chemistry*, vol. v., p. 129.

THE DECOMPOSITION OF CHROMITE BY THE ELECTRIC CURRENT.

By EDGAR F. SMITH.

Two years ago I mentioned* that if finely divided chromite were suspended in melted alkali, and an electric current allowed to act upon the mixture, the mineral would undergo decomposition, its chromic oxide being changed to a soluble alkaline chromate. Details of the experiments made at that time were not published, because difficulties were encountered which necessitated a more careful study of the subject.

The early trials were made with a current of 1 ampère. The oxidation of the mineral was apparently finished in fifteen minutes, but the desire to reduce the time factor, by increasing the strength of the acting current, led me astray. Many successful and unsuccessful decompositions were made before conditions were found which gave satisfactory results. Among other things it was observed that by using a strong current the latter seemed to act chiefly upon the iron oxide and the caustic alkali, liberating larger or smaller quantities of the metal from each. After the decomposition of the mineral had proceeded to a certain extent, the action just mentioned seemed to commence, and undecomposed chromite always remained. Without describing the various modifications that were tried in the hope of obtaining success, I will briefly outline the method which finally gave, and has continued to give, good results.

Method of Oxidation.—Melt 30 to 40 grms. of stick potash in a nickel crucible, 1½ inches high and 2 inches wide; heat gently until the excess of moisture has been expelled. The crucible is then placed upon a heavy copper-wire ring, attached to the anode of a storage-cell.† A small flame is held under the crucible during the entire decomposition. The weighed mineral is carefully brushed from a watch-crystal upon the liquid alkali, the crucible covered with a perforated glass, and the platinum rod, attached to the cathode of the battery, lowered into the melted mass. Set the current in operation; particles of the melted material are thrown against the under-side of the cover-glass, but the liquid soon collects in drops and falls back into the crucible, thus returning any traces of ore that at first may have been projected from the crucible by the bursting of the gas-bubbles.

Experience has demonstrated that it is best to make the crucible the anode; but, before finally interrupting the current, the latter should be reversed by means of a commutator, which, together with an ampèremeter, is always in circuit. The current is reversed for this reason:—metallic iron is deposited upon the cathode and may enclose particles of the ore, removing them from the oxidising field. By reversing the current the imprisoned material is set free and exposed to oxidation.

The quantity of mineral taken for a determination may vary from 0.1 to 0.5 gm. It should be quite fine, although it was never as finely divided as seemed necessary for complete decomposition by other methods. The current employed in the oxidation of the material should not exceed one ampère for the quantities given above. As to the time required for the decomposition, it can only be

said that while the greater part of the mineral is unquestionably decomposed in fifteen minutes, it is best to let the current act for a period of thirty to forty minutes. Much depends upon how refractory the sample under analysis may prove to be. Chromites vary in this respect. It is a difficulty with which all methods must contend. Hence at least one half-hour should be allowed for an oxidation by the electrolytic method. As the decomposition advances the melted alkali acquires a yellow colour. The portion that creeps to the edge of the crucible and about the cover-glass has the appearance of cauliflower.

The current can now be interrupted. Raise the platinum rod (the cathode) from the liquid, remove the cover-glass carefully from the crucible with a nickel tong, rinse its under surface with water, collecting the latter in a beaker. The crucible is lifted from the ring supporting it, and allowed to cool. The platinum cathode should be rinsed with water. It will show a black appearance, due to the metallic iron that had been deposited upon it. It is my plan to dissolve off the iron with dilute hydrochloric acid, to assure myself that undecomposed ore was not present.

When the nickel crucible is cold, place it in a beaker of 300 c.c. capacity, cover with water, and digest upon a warm iron plate. In a few minutes the contents of the crucible can be entirely removed. The liquid now contains the excess of alkali, sodium aluminate, silicate, manganate, chromate, &c. After digesting for some time upon a warm iron plate, filter off the insoluble portion and thoroughly wash it with boiling water. The yellow alkaline solution is now ready for the determination of the chromium.

Treat the residue with warm hydrochloric acid. It should dissolve. It may happen that when quartz is present in the ore there will be a slight residue; but this is immaterial, provided it is not dark in colour. In the analyses given later, the oxides remaining after treating the fused mass with water dissolved completely in warm hydrochloric acid.

Chromium Determination.—This may be made either gravimetrically or volumetrically. In the latter determinations I used the volumetric method almost exclusively. To this end the chromate solution was acidulated with sulphuric acid, and a weighed portion of ferrous sulphate added, the excess being determined with a standardised bichromate solution. Potassium ferricyanide served as an indicator. In several instances the excess of ferrous salt was determined with potassium permanganate. This course, however, was abandoned, as I failed to read the end reaction with sufficient accuracy. By using the volumetric method I believe it possible for the analyst to decompose a chrome ore and determine the chromium content within the space of an hour. Several crucibles can be connected up in the same circuit, and a series of determinations made quite rapidly and with as much accuracy as by any one of our present methods.

Results.

1. 0.1080 gm. chromite gave 51.77 per cent Cr_2O_3 .
2. 0.4787 gm. chromite gave 51.55 per cent Cr_2O_3 .
3. 0.2729 gm. chromite gave 51.23 per cent Cr_2O_3 .
4. 0.1085 gm. chromite gave 51.74 per cent Cr_2O_3 .
5. 0.4184 gm. chromite gave 52.02 per cent Cr_2O_3 .

By the Dittmar method of decomposition a sample of the same ore gave 51.70 per cent Cr_2O_3 .

A second chromite, decomposed by the current, gave as follows:—

6. 0.1515 gm. chromite gave 48.01 per cent Cr_2O_3 .
7. 0.2029 gm. chromite gave 48.34 per cent Cr_2O_3 .
8. 0.3174 gm. chromite gave 48.21 per cent Cr_2O_3 .
9. 0.2071 gm. chromite gave 48.38 per cent Cr_2O_3 .

A portion of the ore oxidised by the Genth method and the chromic oxide determined gravimetrically gave 48.50 per cent Cr_2O_3 .

* *J. Franklin Inst.*, April, 1889; *Ber. d. Chem. Ges.*, xxii., 1019.

† A picture of the apparatus arranged for a decomposition of this kind is given in *Ber. d. Chem. Ges.*, xxiii., 2276; *J. Franklin Inst.*, cxxx., 145; and in the writer's "Electro-chemical Analysis," p. 111.

A light-coloured chromite powder gave the following results:—

10. 0.2012 grm. chromite gave 32.00 per cent Cr_2O_3 .
11. 0.2130 grm. chromite gave 31.50 per cent Cr_2O_3 .

A gravimetric determination of the chromium, after decomposition by the method of Dr. Genth, gave 31.90 per cent Cr_2O_3 .

A fourth specimen of chromite showed the following percentage of chromic oxide, after decomposition by the current:—

12. 0.2295 grm. chromite gave 42.20 per cent Cr_2O_3 .
13. 0.2225 grm. chromite gave 41.70 per cent Cr_2O_3 .

By the Genth method this ore gave 41.30 per cent Cr_2O_3 , while 41.98 per cent Cr_2O_3 was found after a decomposition made by the Dittmar method.

The writer would here acknowledge his indebtedness to Mr. D. C. Wallace for the care and skill with which he conducted the many oxidations that were considered desirable before publishing the facts contained in this communication. — *American Chemical Journal*, vol. xiii., p. 414.

GASOMETRIC DETERMINATION OF OXYGEN IN GASEOUS MIXTURES.

By L. L. DE KONINCK.

THE number of reagents proposed for this purpose is very considerable. Winkler mentions especially hydrogen, phosphorus, the alkaline metals, copper either raised to a high temperature or moistened with hydrochloric acid or ammonia, lead or even thallium in moistened shavings, nitric oxide in the state of gas or dissolved in ferrous sulphate, calcium sulphide, ammoniacal copper chloride, ferrous hydrate recently precipitated (ferrous sulphate and potassium hydrate), sodium hydrosulphite, the alkaline pyrogallates, and white indigo; to which we may add chromous chloride, as proposed by Von der Pfordten.

Most of these substances are, from one or other cause, open to objections. Potassium pyrogallate is the substance most frequently in use, at least for industrial determinations.

But this reagent leaves something to be desired in several respects. As regards exactitude it has the defect of sometimes occasioning the formation of a small quantity of carbon monoxide. It is further extremely alkaline, staining strongly whatever it touches, which renders its use with Bunte's burette disagreeable; and, lastly, its price is very high.

To avoid these different inconveniences we have endeavoured to return to the use of metallic solutions.

We first tried the ferrous salts. The oxidisability of these salts in neutral or acid solutions is so feeble that they do not absorb oxygen completely in a relatively short time. It was necessary to employ them in an alkaline solution, but the addition of alkali produces a permanent precipitate, and the oxidisable matter (the ferrous hydrate formed), being in suspension in the aqueous liquid, does not come in intimate contact with the oxygen to be absorbed.

In order to obtain the ferrous salt in an alkaline solution we had recourse to the tartrates. The reagent was obtained by mixing the following solutions in the proportions given below:—

- A. 40 grms. crystalline ferrous sulphate.
- B. 30 grms. double potassium-sodium tartrate (known as Seignette's salt or Rochelle salt).
- C. 60 grms. commercial potassium hydrate.

Each substance is dissolved in the quantity of water necessary to make up 100 c.c. of solution.

One volume of A is passed into 5 vols. of B; there is formed an abundant whitish precipitate of ferrous tar-

trate, which disappears on the immediate addition of 1 vol. of C to the solution.

We obtain thus a light yellowish solution, which, if exposed to the air, turns green in consequence of the formation of a ferroso-ferric salt, whilst a perfectly ferric salt is also clear.

The order in which the solutions are mixed is not indifferent. If we first mix the potassa and the double tartrate, and then add the ferrous solution, we do not obtain a clear liquid.

The proportions given above have been reached after some trials, from which it appeared that too small a proportion of tartrate produces a dark, or even a turbid, solution. When the proportion of tartrate is sufficient an excess of alkali does not modify the appearance of the liquid.

If used in a double Hempel's pipette for the analysis of air, by means of the Hempel-Winkler burette, graduated in fifths of a c.c., the results showed, as the mean of four determinations, 21.0 per cent of oxygen.

If the pipette is agitated, the rapidity of absorption is very satisfactory; in our experiments the oxygen (in samples of atmospheric air) was completely absorbed in four minutes.

The trials hitherto made with stannous chloride have not given satisfactory results; like the ferrous salts, stannous chloride can only be employed in an alkaline solution. — *Revue des Mines*.

INSPECTION OF CHEMICAL WORKS.

IN the discussion on the Local Government Board Vote, in the House of Commons, on Wednesday, July 15th, Mr. BRUNNER, M.P. for Northwich, said:—"Then there is another matter which I think comes under this vote,—the Inspector of Alkali Works. The law at present is in a very anomalous condition. There are a number of manufactories in the country where the business comes under the designation of Alkali Works. These works carry on operations on a large scale, and are prevented, under the Act, from the discharge of noxious vapours; but, strange to say, in other works, where they use the products made in the larger manufactories, the Act does not apply. In point of fact there are smaller factories using the products of the larger works, and discharging fumes which do quite as much mischief as those which are evolved from alkali works. Oddly enough, if the Inspector can induce the owners of these works to consume these noxious gases instead of turning them out into the air, then the works come under the Act. Those who carry on their work in the most wasteful and harmful fashion are not watched; but as soon as a man ceases doing mischief to his neighbours, then he comes under the watchful eye of the Local Government Board Inspector. If the Right Hon. gentleman (Mr. Ritchie) will consult with the officials of his Department, he will, I have no doubt, find that they are entirely at one with me in this matter, and he may be assured an amendment of the law will have the hearty co-operation of the manufacturers who do come under the Act. So far as the sanitary authorities who understand this matter—more especially in London, where the mischief is rife—are concerned, he may rely upon their support too. I hope the Right Honourable gentleman (Mr. Ritchie) will consider the representation made to him on this subject, and endeavour to put the law into a condition consistent with common sense."

Mr. RITCHIE—"I have to say that the matter has been under our consideration, and a Bill to amend the Alkali Acts has been prepared, and I believe it would meet the views of the honourable gentleman; but there has been no opportunity of introducing it this session. I hope the Alkali Acts will be so extended as to embrace the offending factories mentioned by the honourable member, with regard to which I am quite at one with him."

THE PROGRESS OF CHEMICAL THEORY:
ITS HELPS AND HINDRANCES.*

By Dr. PERSIFOR FRAZER, Prof. of Chemistry.

(Concluded from p. 36).

BERZELIUS believed that the radicles were unchangeable. Liebig and Dumas were not convinced of their entire unchangeability. The two sets of views separated more and more. Liebig finally defined a radicle as one which must be (1) an unchangeable unit in a number of compounds; (2) it must be replaceable in these by simple bodies; (3) it must allow the simple bodies with which it is combined to be replaced by others to form with it new compounds. This was the old radicle theory.

In 1827, J. B. Dumas (1800—1884) commenced a series of researches on the vapour densities of many substances which are solid or liquid at ordinary temperatures, and showed that if Gay-Lussac's law of the identity of atom-weight with gas-volume-weight be true, then some of Berzelius's atom-weights were double and some were half what they should be. This cast doubt on the truth of the law as well as on Berzelius's work, but the latter held fast to his numbers (which were right), and simply confined his employment of the volume theory to permanent gases. The effect upon the minds of chemists, however, was disastrous; for even Gay-Lussac, Liebig, and others despaired of getting any information as to the atoms, and fell back on the equivalents which were shortly afterwards more precisely defined by Faraday as the contemporaneous quantities of the various constituents of compounds which an electric current of given intensity would disengage. This he called the law of constant electrolytic action.

Under the unfortunate fear of having been misled, all attempts at theory were suspended. Gmelin, in the colossal work which bears his name, went back to the apparent weights of combination of Lavoisier's time, and the soul was taken out of the science. But Dumas dealt Berzelius a heavier blow still in the field of organic chemistry in his substitution theory, which he called "metalepsie," of which the two propositions were:—

1. If a hydrogen compound is subjected to the action of chlorine, iodine, or bromine, it takes for every atom of hydrogen lost an atom of one of these elements to replace it.

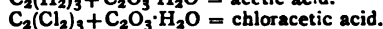
2. If the body contain water, it loses this without replacement.

Auguste Laurent (1807—1853) went further and asserted that the congeries of atoms called radicles which had suffered this substitution of H by Cl, or the loss of water, remained practically the same in properties. This was called the nuclear theory, which was short-lived, but before it had quite disappeared from the field, Dumas came forward with his discovery of chloracetic acid, and declared himself for Laurent.

He maintained that the newly-formed body in such substitutions must resemble the old, and he classed such original and substituted products together as derivable from the same type. This is called the old-type theory to distinguish it from the new-type theory subsequently set up by Laurent and Gerhardt. Dumas showed that his trichloracetic acid, in spite of the substitution of six atoms of chlorine for six atoms of hydrogen, was similar in its behaviour and characteristics. He stated that "in organic chemistry there are certain types which remain constant even when one substitutes an equal volume of Cl, I, and Br for their H." Acetic and trichloracetic acid, aldehyd and chloral, marsh gas and chloroform, belong to the same chemical type. He went so far as to assert that all bodies derived from each other by equivalent substitutions belonged to the same "mechanical type." This was followed by the following declaration

of war against Berzelius's dualistic theory. "Every chemical compound forms a complete whole, and does not consist of two parts. Its chemical character depends principally upon the number and arrangement of its atoms, and secondarily upon their chemical nature."

Berzelius was obliged to account for the facts discovered and to conform his explanation to the new discovery of Melsens in 1842, that chloracetic acid was reduced to acetic acid by potassium amalgam. He finally decided to do this by supposing that—



In other words that acetic acid consisted of a radicle (C_2H_6), and trichloracetic acid of the corresponding radicle (C_2Cl_6), each respectively paired with oxalic acid ($C_2O_3 \cdot H_2O$).

But in doing this he gave up the very principle that he had been contending for, viz., that the radicles were unalterable, since it was evident that in the first two symbols of the formulae a radicle C_2H_6 had been changed by substitution into C_2Cl_6 .

This admission weakened the faith of his most admiring followers, and threw the blight of timidity over the speculations of chemists for thirty years. And yet withal, Berzelius was right in almost every important generalisation which he made, and right (within the resources of his time) in every constant he established. Chemistry without his contributions would yet be a mere scaffolding.

The history of this controversy, the most important which has taken place since the commencement of the modern science, is useful as an illustration of another kind of hindrance to the progress of intelligent theory. It is a too-blind devotion to one man, and despair of attaining the object which he strove for if he has failed. It is true that if ever hero worship were justifiable, that of Berzelius was, but to sweep aside the whole fabric of his labours because part of his theory was proved untenable was the veriest cowardice and injustice to him.

How many a chemist in the last forty-five years has struggled through a jungle thick planted with the pretty crochets of mediocre men, wondering what all this jargon meant and whither it was tending; deprived of the vivifying influence of a high and noble thought, and condemned to delve and grub without reasoning, because one of the greatest geniuses of original research the world has ever seen was worsted in an encounter on a small part of his field, and a part to which he had not devoted the best of his thought!

Among the most innocent looking hindrances to the development of sound chemical theory must be reckoned an hypothesis which was given anonymously to the world in 1815, and which was later referred to its true author, Dr. Prout. This was the supposition that the atomic weights of all elements were even multiples of that of hydrogen.*

No argument was offered to show why this should be true, but it had the specious and enticing appearance which captivates that sense of order which is a human instinct.

Prout did not hesitate to add the obvious conclusion that hydrogen was the original material, or as one of the greatest of living chemists has put it, the prototype.

By the usual rule which exists in such cases, Prout should not have had credit for anything more than a pretty idea, which, besides, was only a modification of a similar thought of Thomson, the collaborator of Dalton, who believed that the atomic weights of the elements were multiples of that of oxygen. Prout was more nearly right, of course, because the weight of hydrogen is only about one-sixteenth as great as that of oxygen, and is a more general divisor. But in spite of all, this pretty thought strongly influenced many admirable chemists,

* Introduction to the Chemical Lecture Course at the Franklin Institute, November 10, 1890.

* It should be stated that Profs. Crookes, F. W. Clarke, and other chemists of the first rank still show a leaning towards the acceptance of something like Prout's "law."

even those like Dumas and Stas and Marchand and Erdmann, whose labours in accurately determining atomic weights did more than all else to prove the baselessness of Prout's assumption.

Even to-day the tendency is manifested to get back to the even numbers which Leopold Gmelin adopted in his great work, in entire disregard of the accurate results of Berzelius. It must be added that some are prevented from falling into this snare through the hope that the real protyle will be some day discovered, and that being lighter than hydrogen it will provide a table of atomic weights less disfigured by fractions than the present one.

The moral of this theory is that healthy scientific work must not be influenced by premature attempts to put a finish on it and make it appear symmetrical.

The discovery of an element lighter than hydrogen and possessing properties which, as it will be seen, we can to a certain degree predict, might render very desirable those ugly decimal affixes to the present atomic weights in order to show that experiment supported theory. On the whole, Prout's "law," as it is called, is a hindrance, and quite an annoying one.

The downfall of dualism and the establishment of unitism in compounds was followed by a storm of conflicting notions of chemical union, into all of which it is not necessary to enter.

To Laurent and Gerhardt is due the praise for unifying in the new theory of types the opinions which had been previously thought to be diametrically opposite. It has been said that the uncertainty which prevailed upon the overthrow of the dualistic theory of Berzelius caused most chemists to go back to the old equivalent weights $O=8$, but Gerhardt opposed this weakness and strongly maintained the correctness of the numbers of Berzelius, merely correcting his early atomic weights for the alkaline metals in conformity with the then acquired knowledge of the existence of two atoms of the metal in the alkalies. He showed that the quantities of H_2O , CO_2 , &c., separated in the reactions of organic compounds did not represent one equivalent each, but two. His aim was to reduce all formulæ to one criterion, which in the case of gaseous substances, was two volumes. His view was, that when two bodies react, one constituent of one (H), uniting with one constituent of the other (O), leaves two residues which unite. Hofmann discovered the substitution products of ammonia and thus established the ammonia type. Williamson established the water type and referred alcohols, ethers, acids, bases, and salts to this type. Gerhardt recognised the hydrogen type, the water type, and the ammonia type, but considered the compounds under them units and not couples.* Laurent explained the atom as the least part of matter that can take part in chemical combination; the molecule as the least part which can exist alone, and the equivalent of elements as those quantities which would perform the same amount of chemical work.

Thus the new type theory was a compromise skillfully constructed to save the Berzelians from chagrin while embodying all of value in their system. It took the idea of type from Dumas, that of radicle from Berzelius, but with the difference that it did not presuppose the groups of atoms called radicles to be necessarily capable of existing alone. Gerhardt admitted that the elements substituted in radicles did change the character of the compound.

Kekulé, in the year of Gerhardt's death (1857), added the conception of mixed types.

It is unnecessary to pursue this branch of the theory farther. An entirely new discovery appeared which was

a welcome light and enabled many of the obstacles in the way of progress to be seen and surmounted.

Frankland, after an investigation of the alcohol radicles, first announced his views of valence in 1853.

Kolbe, in 1855, accepted his theory and declared that the fatty acids, if imagined free of water, were derivatives of CO_2 or C_2O_4 in which one atom of oxygen is replaced by C_2H_3 .

Frankland's discovery was really a corollary of multiple proportions, and had been vaguely foreshadowed by Wöhler, who said that one atom of antimony was equal to three of hydrogen.*

It is simply, as Hofmann expresses it, chemical value in exchange. Some elements, of which H is a type, can only combine one atom to one atom; some, like oxygen, can hold two atoms of the first-named kind in union. Some, like nitrogen, can hold three, and some, like carbon, four. Kekulé, in 1858, determined this valence of carbon, added another to the list of types which led to the establishment of the ring structure of some organic compounds.

Erlenmeyer found that every element had a highest valence, but might not use all of its combining powers. Wurtz and Naquet believed the valence changeable, Kekulé believed it fixed, and that only compounds using all the valences of every constituent were real chemical compounds. It appears to be the general opinion now-a-days that the valence of elements is not only variable, but that it does not even vary, as was supposed, by the suppression of two affinities at once (which might be explained as the loss or suppression of two opposite polarities); but that an element may be now an triad and now a perissad, i.e., even or odd in the number of its bonds.

The subject is not well understood, but it presents a good opportunity for adding on the lesson taught by Prout's "law," not to be captivated by a beautiful idea, but to stick closely to facts.

It would be impossible at this time to follow all the subsequent contributions to the theory of chemistry, but the most superficial sketch of the subject would be incomplete without studying an extraordinary discovery of which the advent had been preparing long before its announcement by Lothar Meyer and D. Mendelejeff. The latter pointed out that if the atomic weights of the light elements (or those with atomic weights from one to thirty-six) be arranged in two lines of seven each, a natural grouping is effected, thus:—

Li—7. Be—9·4. B—11. C—12. N—14. O—16. F—19.
Na—23. Mg—24. Al—27·3. Si—28. P—31. S—32.
Cl—35·5.

In these two lines two periods are passed over. From left to right in each, with the increase of atomic weight is a change from the most electro-positive to the most electro-negative, while the elements in the centre are nearly neutral. Again, from the beginning of the second period, elements of the same kind come to stand under one another. The same might be shown to be true in their behaviour in forming compounds with oxygen. Again the metals are on the left and the non-metals on the right. The specific gravities increase, and the atom volumes (or the atomic weights divided by the specific gravities), and all other physical and chemical properties which have been examined, change by regular gradations in vertical or horizontal lines. Without pursuing this subject into its curious details it is apparent that there has been some law exemplified in the production of these elements; a condition of things which is cyclical in its action or, as it is called, periodic. From the data obtained it was possible to construct a table which, while containing all the known elements, contained gaps in certain places where (according to the analogy of the periods), elements

* Dr. Wolcott Gibbs, in 1858, after referring to his attribution of the theory of water types to Gerhardt and Williamson, says: "I have not done justice to T. Sterry Hunt, to whom is exclusively due the credit of having first applied the theory to the so-called oxygen acids and the anhydrides; and in whose earlier papers may be found the germs of most of the ideas on classification usually attributed to Gerhardt and his disciples."—*Chem. and Geol. Essays*, p. 468.

* Von Meyer's admirable and impartial work on the History of Chemistry (Leipzig, 1889), a most valuable contribution to the science and a fitting supplement to Kopp's, has been largely drawn upon.

ought to have been, but none had been discovered. From the position of these gaps it was even possible to prophesy from the analogy of elements in similar positions of other periods, that, if discovered, the new elements filling these gaps would have properties intermediate between those occupying places before and after it, in regard to fusing point, solubility, specific heat, positive or negative polarity, &c.

After the announcement of this periodic law, chemists were impatient for a verification of its accuracy, and in the discovery of the newest metals, gallium and germanium, those predictions were found to have been well founded.

As no better test of a theory can be had than its use as a basis of prediction, the periodic law may be said to have been proved, and to be evidence of a profound and intimate connection between the elements.

What the connection is has not been certainly ascertained, but a bold and beautiful hypothesis was enunciated in 1886, by one of the greatest of the master minds of our age, in his Presidential Address before the Chemical Section of the British Association for the Advancement of Science, William Crookes.*

A skeleton of the views in this paper is as follows:—

Norman Lockyer said that a terrestrial element is an exceedingly complex thing, broken up into simpler things at the temperature of the sun.

Sir Benjamin Brodie in 1867 said, "We may conceive that in a remote time or in remote space there existed formerly, or may exist now, certain simpler forms of matter than we find on the surface of our globe."

Professor Stokes, in referring to a line in the spectrum of the nebulae, remarks:—It may possibly indicate some form of matter more elementary than any we know on earth."

Crookes holds that the unequal distribution of elements in the earth's crust is evidence in favour of their composite nature.

The probability of such rare metals as yttrium, ytterbium, &c., having been brought together by chance in a few uncommon minerals and in a few localities, is very small. They would rather seem to have been formed severally from some common material placed in conditions in each case nearly identical; and the existence of other groups of metals, as nickel, cobalt, and the two platinum groups furnishes additional ground for this supposition. Another argument in favour of their composite nature is that of the organic compound radicles.

Dr. Carnelley at the previous meeting (1885) had shown that on the supposition of two chemical elements, one with an atomic weight of twelve and the other of two—all the features of periodicity in Mendeleeff's series could be produced by their combination, and every well known element reproduced except hydrogen.

Dr. E. J. Mills considered the elements we now have as the result of successive polymerisations.

All these observations Crookes has thrown into a diagram by which is represented the hypothetical condensation of the original "fire mist," out of which the universe was derived, and which contained not matter but the potentiality of matter. In this condensation due to the gradual lowering of the temperature, another force than that of heat was at work—a force which he supposed not very different from electricity. As the temperature was lowered the elements congealed one by one out of the protyle in the form of atoms, of which the weight depended upon the temperature at the time of this formation, and the properties due to the electrical phase at the time of their birth. But the potential energy of the atom was greatest in the first that were thus condensed and more sluggish in the last when the temperature was lowest and the electrical force least.

We must be warned by the very beauty of this con-

ception that it is but the effort of a superior mind to materialise for us the successive phenomena which it sees in imagination, and not a register of observed phenomena or a proven genesis. Yet it is impossible to conceive of the regularity and accuracy with which the labour of a century is fitted into that scheme without feeling that it contains more than a figment of the fancy.

At least nothing greater and nobler has been attempted in our science since its inception, and whether it be finally assigned its place among the great theories of the world or not, it will, undeniably, through its broadening of our views and its enlarging of our conception, have been a help to the progress of chemical theory.

NOTICES OF BOOKS.

The Foundations of Chemistry. (Grundlagen der Chemie).

By D. MENDELEJEFF, Professor in the University of St. Petersburg, Translated from the Russian by L. JAMIN and A. THILLOT. St. Petersburg: Ricker, 14, Nevsky Prospekt. (Large 8vo.)

THIS work is certainly not one of those voluminous compilations which aim at telling us everything that has been ascertained in chemical science. Still less is it a cram-book from which the intending examinee may gain a superficial varnish of knowledge, which it is hoped will satisfy the requirements of some Board or Department. Its *raison d'être* lies in presenting a condensed but clear view of the philosophy of chemistry.

The Introduction opens with the words—"Chemistry concerns itself with the investigation of the homogeneous substances of which all bodies of the world are composed." Two words here, "investigation" and "substances," words which the many hear, read, or use without attention, are made the subject of two suggestive notes. Says the author, "If anything is to be explored, something else must be assumed as given without investigation or as already known." As examples he gives the axioms of geometry and the faculty of organisms to reproduce themselves,—a concept which is for the present inexplicable.

We cannot refrain from envying those nations which can use, in place of our "phenomenon" and its paronymes, a word "understanded of the people," and incapable of being juggled with. It is not soothing to our feelings to hear quacks boasting of their success as "phenomenal."

In classifying the Sciences, Prof. Mendeleeff—like some other Continental authorities—uses the word "biology" in a different acceptation from that which prevails amongst us. He speaks of "physiology" and biology, while with us biology is a whole of which physiology is one part.

The author distinctly recognises Lavoisier as the founder of modern chemistry, and as fully recognises that "matter is neither created nor destroyed." He insists that the highest scientific reputation must be ascribed not to the man who first announces a truth, but to him who can secure its recognition. But such men can arise only in consequence of the work of many others, and by means of long accumulation of materials.

It will be remarked that Prof. Mendeleeff is distinctly opposed to the rising doctrine of transmutability of the elements. If such conversions were possible we might, he holds, expect to find the simple bodies undergoing mutual transmutations. Such expectations, however, are contrary to the very essence of transformation, whether among elements or organisms. We consider existing animal species as having been developed not from each other, but from earlier less-differentiated forms. In like manner we do not seek to derive iodine from bromine or chlorine, but to trace all the members of this group from

* See Address of William Crookes, President of the Chemical Section Brit. Assoc. for the Adv. of Science, at the Birmingham Meeting, 1886. (Report B. A. S., 1886, p. 558.)

some primæval generalised halogen. That we are not yet able to prove how the elements have been formed from one original matter, protyle, may be conceded.

The author asserts that "it has been established by spectral analysis that the simple bodies exist on the most remote stars." True; but the astrophysicists teach us that the number of kinds of simple bodies is smallest in the white stars, which we have reason to suppose are the hottest, but is larger in those of presumably lower temperatures. Hence it seems fair to infer not that certain "elements" are decomposed by the highest temperatures, but that they are only formed as a star gradually cools down.

Concerning some of the recognised or supposed simple bodies the author entertains doubts,—*e.g.*, erbium, terbium, samarium, neodymium, &c. He thinks that they may consist of mixtures of other known bodies.

Regarding chemical affinity and its laws Prof. Mendeleeff writes:—"As regards the chemical mechanism and the molecular world, Lavoisier and Dalton may be compared with Copernicus and Kepler; its Newton has not yet appeared."

Concerning solutions the author is of opinion that the unity of our chemical concepts cannot be reached so long as a physico-mechanic view predominates concerning indefinite compounds (*e.g.*, solutions). "In seeking to bring solutions under the concepts of the Daltonian atomic theory, I hope to arrive not only at a comprehensive and harmonious chemical theory, but to give an impulse to new researches and observations which may either confirm this view or substitute for it a more complete and a simpler theory."

This book is entitled to many and attentive readers, and few will rise from its conscientious perusal without profit. They will find in the author a judicious and thorough guide through the widening fields of chemical philosophy.

CORRESPONDENCE.

ESTIMATION OF FATTY MATTER IN TURKEY-RED OIL.

To the Editor of the Chemical News.

SIR,—Mr. Williams finds my process to be inaccurate (see CHEMICAL NEWS, vol. lxiv., p. 15) when compared with his wax method, and against three samples of prepared oil containing theoretical percentages of fatty matter; but he gives no details as to how the theoretical fatty matter in these samples were found or calculated. Mr. Williams has also made the mistake of using 5 c.c. of 1 to 2 HCl instead of 0.5 c.c. of 1.2 sp. gr. HCl,—a point of some importance,—and charges me with the grave error of not comparing the ether extraction method with some standard process. Where is the standard process to be found? Is it the wax process? My modified process, like Mr. Williams's, requires very careful working, and, when carefully carried out, I believe there is little or no decomposition of the fatty matter.—I am, &c.,

J. A. WILSON.

Tottington, July 15, 1891.

ESTIMATION OF ALUMINIUM IN CAST-IRON.

To the Editor of the Chemical News.

SIR,—I notice in CHEMICAL NEWS (vol. lxiii., p. 172) a method, by M. A. Carnot, for the estimation of aluminium in cast-iron and steel, which is substantially the same as that originally described by Mr. Stead. M. Carnot does not in any way allude to Mr. Stead's method, and I think

it is only fair that the attention of your readers should be called to this fact.—I am, &c.,

A. S. BLECKLY.

The Laboratory, Bewsey Forge,
Warrington, July 2, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 1, July 6, 1891.

Study of Carbon Tetraiodide.—Henri Moissan.—Boron triiodide furnishes several new reactions. On projecting boron iodide into dry, cold chloroform, the iodide is dissolved and the mass quickly congeals. After a few days the gelatinous matter disappears and the bottom of the vessel is filled with a fine crystallisation of iodoform, whilst vapours of boron chloride escape continuously. Phosphorus reacts energetically upon boron iodide. If we prepare a solution of boron iodide in pure dry carbon disulphide, and add ordinary phosphorus free from water, there is produced a dense reddish powder, from which, on heating, there is evolved a small quantity of phosphorus and phosphonium iodide. The residue is a white powder containing phosphorus and boron. This boron phosphide, infusible at a red heat, is not acted on by nitric monohydrate. It is decomposed by watery vapour into hydrogen phosphide and boric acid, and resembles in its properties the boron nitride of Deville and Woehler. If boron triiodide is permitted to react upon carbon tetrachloride there is readily obtained boron trichloride and carbon tetraiodide. This compound, when very dry, if heated *in vacuo* to between 90 and 100°, sublimes very slowly in fine red crystals, having the lustre and the transparency of the synthetic rubies of Fremy and Verneuil. Their composition is represented by the formula C_2I_4 .

Combinations of Camphor with the Aldehyds: New Method of Forming the Alkoylcamphors.—A. Haller.—This paper does not admit of useful abridgment.

Calculation of Molecular Volumes.—G. Hinrichs.—The author describes a statical and a dynamical method which agree in their results.

An Explosive Compound formed in the Action of Baryta-Water upon Chromic Acid in Presence of Oxygenated Water.—E. Péchard.—There is produced a precipitate of a chamois colour, which when dry detonates violently if struck or heated. Its composition is possibly BaO_2CrO_3 .

Determination of Small Quantities of Boric Acid.—F. Parmentier.—The waters upon which the author has experimented were evaporated, when they give rise to precipitates insoluble in water, and containing all the boric acid, along with the chief part of the silica, the phosphoric acid, and the arsenic. On treatment with hydrochloric acid they yield liquids which, if evaporated at low temperatures, do not lose any boric acid. The matter on being taken up in water acidulated with hydrochloric acid, and then treated with ammonium nitrate slightly ammoniacal, leave a residue containing the iron, alumina, manganese, arsenic, and phosphoric acid, whilst the boric acid remains in solution. The liquid is rendered distinctly acid either with dilute sulphuric or hydrochloric acid, and is then divided into two exactly equal portions. In one of these portions the acidity is determined, using helianthine as an indicator, whilst in the other a similar acidimetric determination is effected with the tincture of litmus as prepared by De Luynes. The nor-

mal alkaline liquid used is caustic soda. The quantity of boric acid is deduced from the difference of the results obtained in the two operations. The change of colour with litmus takes place when sodium baborate has been formed.

Journal für Praktische Chemie.
New Series, Vol. xliii., Parts 7 and 8.

Further Observations on the "Black Sulphur" of Magnus.—Fr. Knapp.—The preparation of Magnus contains sulphur certainly in two different conditions; the one part as an integral constituent of the process of carbonisation, the other in the free condition. The free sulphur cannot possibly be the ordinary yellow kind, differing totally in its behaviour. The temperature at which it is converted into vapour is much higher than the boiling-point of yellow sulphur; its vapour is not brown but colourless, and when heated with access of air it yields sulphurous acid before the appearance of a visible red heat, and without any phenomena of combustion.

Researches from the Laboratory of the University of Freiburg.—These researches comprise papers by Ad. Claus on the constitution of benzol, by Ad. Claus and E. Krause on thymol, and by Ad. Claus on the formation of alkyl-ketones from the halogen derivatives of aromatic carbon-compounds.

On the Betaines of the Pyridine Bases.—Martin Krüger.—By means of the methods of Hofmann and Liebreich the betaines of pyridine, β -picoline, and ethyl piperidine can be very conveniently obtained. The betaines of the pyridine series approximate in their entire behaviour to the betaines of the fatty series.

The Derivatives of Salol.—W. Knebel.—The compounds examined are acetylsalol and the nitro-derivatives of salol.

The Addition of Sodium Acetacetic and Sodium Malonic Ethers to the Ethers of the Non-Saturated Acids.—Michael and Paul C. Freer.—The continuation of an extensive memoir.

The Faculty of Reaction of Monochlorotrimethylene and Certain Allied Compounds.—E. Gustavson.—These experiments show that among all the isomers of the formula C_3H_5Cl hitherto examined in this direction, monochlorotrimethylene is the most stable if exposed to the action of alcoholic potassa.

A New Quantitative Separation of Manganese and Zinc.—P. Jannasch and J. F. Gregory.—Already inserted.

On Dimolecular Cyanethyl.—P. S. Burns.—The author has submitted dicyanethyl to the action of acid chlorides and of hydroxylamine. The investigation is not yet complete.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xiv., No. 2.

Gasometric Determination of Oxygen in Gaseous Mixtures.—Prof. L. L. de Koninck.—(Inserted at p. 45).

Volatility of Iron.—Dr. Fleitmann.—Experiments on soldering together iron and nickel have led the author to important results on the volatility of the former metal and its atomic penetration. The adherence of the two metals was such that it was impossible to separate them by mechanical action, and chemical analysis demonstrated a true alloy—an intimate combination, although the soldering had been effected at a temperature 500 or 600° below their point of fusion. Other experiments proved the volatility of iron at a cherry red heat. Two superimposed plates of iron and nickel having been submitted to a similar heating, the iron passed over to the nickel in notable quantity without either soldering or adhesion of

the surface. Over the entire sheet of nickel there was formed an alloy of iron, which in sheets of 1 m.m. penetrated to 0.05 of their thickness, and contained a mean of 24 per cent of iron. This passage of iron to nickel is not reciprocal. This volatility of iron is still unexplained, and we do not know whether it is due to traces of ferric cyanide, chloride, or carbide.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vi., No. 62.

Communications and Reports presented by M. Davanne on the Present Applications and Procedures of Photography.—The author recognises in photography three stages; the first, that of the Daguerre plate, the second, that of collodion and its derivatives, and the third, or present phase, characterised by the exclusive use of silver gelatino-bromide. He ascribes the early failures in the use of bromine preparations to the employment of silver bromide alone, to the action of yellow light, and to the absence of an excess of soluble bromides. In a report made by M. Davanne on behalf of the Committee of Constructions and the Fine Arts it is proposed to dispense with the lens, using in its stead merely a fine hole. Further reports by the same author treat of photography in balloons, of aerial photography by means of kites, and on the "Obturator" of MM. Londe and Dessoudeix.

Basic Slags: their Use in Agriculture.—M. Campredon.—The writer upholds the employment of basic slag as a phosphatic manure, but points out that to be a "complete manure" it requires the addition of potassa and of nitrogenous matter. He does not consider the iron and manganese oxides as injurious.

Vaseline, Petroleum.—M. Riche.—An account of the uses of the mineral fats in pharmacy. Its abuses in confectionery, &c., and the means for its detection in articles of food are not referred to.

MISCELLANEOUS.

The Atomic Weight of Lanthanum.—Bohuslav Brunner (*Ber. der Deutsch. Chem. Gesell.*).—The author determined this atomic weight of lanthanum by converting lanthanum oxide into sulphate, and obtained the following result: $La(O=16)=138.21$. This value is identical with those obtained by Cleve (*Bull. Soc. Chim.*) and Bettendorff (*Ann. Chem. and Pharm.*). The material was obtained from impure lanthanum oxide by fractionated exhaustion with ammonia nitrate, and contained therefore the most positive earth of cerite. It was totally free from "didymium," and displayed in the spark spectrum of the chloride no lines belonging to other earths. The author adds in a note, "I designate as didymium the mixture which in addition to neodymium and praseodymium certainly contains other earths."

ERRATA.—P. 33, col. 1. At the International Congress of Hygiene and Demography, the paper to be read by Dr. Russell is entitled "Town Fogs and their Effects," and that by Sir A. Mitchell and Dr. Buchan "The Influenza and Weather of London."

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THE CHEMICAL NEWS.

VOL. LXIV., No. 1653.

ON THE NATURE OF SOLUTION.

(No. III.).

By J. ALFRED WANKLYN and WILLIAM JOHNSTONE.

CONTINUING the investigation, we are now prepared to announce that we have found a new chemical, or physico-chemical, function of wide generality, viz., $i - i_1$ = the condensate. It is the quantity of water condensed by one grm. of a substance when that one grm. enters into the 100 c.c. or the litre of solution, and *not* overflowing out of the 100 c.c. or the litre, as it would do in the case of sugar.

Our investigation is now sufficiently advanced to enable us to say that the condensate bears an atomic relation to the substance dissolved. The condensate is also quite distinct from water of crystallisation. In the instance of the sulphates, the condensate is large, but it is not the same as the water of crystallisation. We expect that the salts of each particular alkali will be characterised by the condensate belonging to the different salts. The following is a tabular statement of soda and potash salts:—

Soda Salts.

	Found.	Theory.
2NaCl + H ₂ O	0·140	0·153
3NaBr + H ₂ O	0·054	0·058
3NaI + H ₂ O	0·042	0·040
4NaHO + 5H ₂ O	0·568	0·562
3NaNO ₃ + 2H ₂ O	0·146	1·141
Na ₂ OSO ₃ + 2H ₂ O	0·281	0·253
3NaHOCO ₂ + 2H ₂ O	0·132	0·143

Potash Salts.

	Found.	Theory.
3KCl + 2H ₂ O	—	—
3KI + H ₂ O	0·035	0·036
3KNO ₃ + H ₂ O	0·058	0·059
3KClO ₃ + H ₂ O	0·063	0·049
2K ₂ OSO ₃ + 3H ₂ O	0·152	0·155
2KHOCO ₂ + H ₂ O	0·097	0·090
KHO + H ₂ O	0·341	0·321

and here follows some of the experiment details.

Iodide of Potassium.

The specific gravity of a solution containing 10·00 grms. per 100 c.c. of solution was 1·07020.

$$\begin{aligned} i &= 0·702 \\ i_1 &= 0·667 \\ \hline i - i_1 &= 0·035 \end{aligned}$$

3KI + H₂O requires $i - i_1 = 0·036$.

Chlorate of Potash.

Specific gravity of the solid was found 2·132 at 21° C. A solution containing 5·00 grms. per 100 c.c. had specific gravity 1·02970.

$$\begin{aligned} i &= 0·594 \\ i_1 &= 0·531 \\ \hline i - i_1 &= 0·063 \end{aligned}$$

3KClO₃ + H₂O requires $i - i_1 = 0·049$.

Bicarbonate of Potash.

Specific gravity of the crystals found 2·104. A solution

containing 10 grms. per 100 c.c. had specific gravity 1·06220.

$$\begin{aligned} i &= 0·622 \\ i_1 &= 0·525 \end{aligned}$$

$$i - i_1 = 0·097$$

2KHOCO₂ + H₂O requires $i - i_1 = 0·090$.

Caustic Potash.

The specific gravity of solid caustic potash was found to be 2·00 at 20° C. The specific gravity of a solution of caustic potash containing 10 grms. KHO in the 100 c.c. of solution was 1·08415. Therefore—

$$\begin{aligned} i &= 0·841 \\ i_1 &= 0·500 \end{aligned}$$

$$i - i_1 = 0·341$$

KHO + H₂O requires $i - i_1 = 0·321$.

Caustic Soda.

The specific gravity of the solid was found to be 1·923 at 20° C. A solution containing 3·68 grms. per 100 c.c. had a specific gravity 1·03930. Therefore—

$$\begin{aligned} i &= 1·068 \\ i_1 &= 0·480 \end{aligned}$$

$$i - i_1 = 0·588$$

4NaHO + 5H₂O requires $i - i_1 = 0·562$.

Caustic Lithia.

Specific gravity of the solid 1·495 at 20° C. A solution was made and its specific gravity taken.

$$\begin{aligned} i &= 0·924 \\ i_1 &= 0·331 \end{aligned}$$

$$i - i_1 = 0·593$$

LiHO + H₂O requires $i - i_1 = 0·750$. 5LiHO + 4H₂O requires $i - i_1 = 0·600$.

We are prepared with a further theoretical development illustrated by the case of sulphate of copper, and can now show a *completed* volumetric relationship.

The Laboratory, 13, Fish Street Hill, E.C.
July 20, 1891.

COLORIMETRIC METHOD FOR ESTIMATING GALLOTANNIC ACID, GALLIC ACID, AND TANNIC ACID IN BARKS, &c.

By SAMUEL J. HINSDALE, Fayetteville, N.C.

DISSOLVE 0·04 grm. potassic ferricyanide in 500 c.c. water, and add to it 1·5 c.c. (about 22 drops) liquor ferri chloridi. Call this *iron mixture*. (The best way to prepare this is to dissolve 0·4 grm. potassic ferricyanide in 500 c.c. water, and make 50 c.c. of it up to 500 c.c. and add the liquor ferri chloridi.)

Dissolve 0·04 grm. "pure tannin" (gallotannic acid) which has been dried at 212° F. in 500 c.c. of water. Call this *tannin solution*. (The best way to prepare this solution is to dissolve 0·4 grm. of the dry gallotannic acid in 500 c.c. water, and make 50 c.c. of it up to 500 c.c. with water.)

Exhaust 0·8 grm. oak-bark with boiling water, and make it up to 500 c.c. with cold water. (It is well to exhaust 8 grms. of the bark, and make the infusion up to 500 c.c., and take 50 c.c.—equal to 0·8 grm. bark—and make it up to 500 c.c. for the assay.)

Place six 2-ounce clear glass tumblers (or beaker glasses) on a white surface, and in one of them, *with a dropping pipette* (about four inches long and one-quarter inch wide) *about half filled*, put *five drops* of the infusion of bark, and in the others, *with the same pipette* (after

rinsing), put 4, 5, 6, 7, and 8 drops of the "tannin solution." (The drops of the infusion and of the "tannin solution" must be uniform. The use of the same pipette, about half filled, *insures that.*) (The pipette should be made so as to deliver *about* 50 or 60 drops per minute, 20 drops of which should weigh *about* 1 grm.)

Now add to each about 5 c.c. of "iron mixture" (it is convenient to have a measure for this—a homœopathic vial will answer), and in about one minute add to each tumbler about 20 c.c. water, and *within three minutes* observe the shades of colour. The number of drops of "tannin solution" used in the tumbler which corresponds in shade of colour to the tumbler containing the infusion of bark *indicates the percentage* of gallotannic acid in the bark,—*i. e.*, if it is the one in which seven drops were placed the gallotannic acid strength of the bark is *seven per cent.*

It is best to observe the shades of colour horizontally rather than vertically, and to hold up the infusion tumbler, with the one which most nearly corresponds, opposite to a white wall, with your back to the light.

The above is written for *oak bark*, but the same process will answer for any substance containing less than 10 per cent of gallotannic acid.

For substances containing between about 10 and 20 per cent it is best to dilute the infusion with an equal part of water and proceed as above, using *five drops* of the *dilute* infusion, and for the answer double the result. Thus, if the diluted infusion of tea required eight drops of "tannin solution" to correspond, call the percentage *sixteen*.

For substances containing less than 1 or 1½ per cent, exhaust *eight grms.* instead of 0.8 grm., and take *one-tenth* of the result for the answer. For substances containing more than 20 per cent—as galls, sumach, catechu, &c.—you may dilute the infusion with two, three, or more times its bulk with water, and calculate as above (as with tea), or you may use one, two, three, or four drops of the undiluted infusion in the first glass, and make the calculation thus:—*i. e.*, As the number of drops of infusion used is to the number of drops of "tannin solution" used (to correspond), so is 5 to the answer; thus, suppose *two* drops of infusion were used, and the corresponding tumbler contained *fifteen* drops of "tannin solution"—2 : 15 :: 5, answer 37.5 per cent.

The object in diluting the infusions is because the infusion glass may be of too deep a blue shade. It is better that it should just produce a *light* blue.

The tumblers must be perfectly clear and clean.

The "iron mixture," "tannin solution," and infusion must be freshly prepared, and not exposed to the rays of the sun. The water used must be free of iron and tannin.

The above was published in the *American Journal of Pharmacy*, March, 1890, and is for the estimation of *gallotannic acid* only.

The same method can be used for the estimation of *gallic acid*; and by deducting the percentage of *gallic acid* found from the percentage of *gallotannic acid* found, the percentage of *tannin* in the bark can be determined with much accuracy.

To estimate the *gallic acid* (having previously estimated *gallotannic acid*), precipitate the *tannin* from 50 c.c. of the infusion—equal to 0.8 grm. bark—by mixing with it 0.2 grm. alum and 20 c.c. solution of gelatin (3 grms. to litre). After mixing well, make it up to 250 c.c. with water, and filter off a little of it. Put five drops of the filtrate in the first glass, and proceed according to the method, using a solution of 0.02 grm. pure dry *gallic acid* to a litre of water, in place of the "tannin solution." (To prepare this solution, dissolve 0.2 grm. of the *gallic acid* in 500 c.c. of water, and make 50 c.c. of it up to a litre, with water.)

One-eighth of the number of the drops of the *gallic acid* solution used to produce the same shade of colour

as is produced in the glass containing the filtrate will indicate the percentage of *gallic acid* in the bark, which, deducted from the percentage of *gallotannic acid* found, will tell the percentage of *tannin* in the bark.

Barks vary very much in *gallic acid* strength; for instance, white oak contains from 2 to 2.5 per cent, while hemlock contains only about 1 per cent.

It is all important that the solutions and the infusion be freshly prepared. The "iron mixture" is decomposed a little in twenty-four hours. It must not be exposed to the rays of the sun. The "tannin solution" changes in a few days. This solution must be made with pure *gallotannic acid* which has been dried at 212° F.

The infusion of bark undergoes some change in a few days.

The glasses used must be clean and clear, and placed on a white surface.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 41).

X.—Manganese.

1. With oxalic acid. Star-shaped aggregates of prismatic twin crystals, measuring 100–120 micro. Oblique terminal plane of 60°. Straight extinction. Single crystals in presence of zinc, cobalt, and nickel. Alkaline salts interfere, and strong acids more so. Limit of the reaction about 0.001 m.grm. With potassium oxalate about 0.0005 m.grm.

2. With phosphoric salt and ammonia. Hemimorphous crystals of the rhombic system of 40 micro., similar to those of ammonium magnesium phosphate. Limit at 0.0005 m.grm. Mn.

On account of the rapid oxidation of ammoniacal solutions of manganese, the port-object must be heated with the acid manganese solution, and the mixture of phosphate and ammonia added subsequently. For closer examination the crystals adhering to the glass may be rinsed off, and potassa or soda-lye be added along with a drop of hydrogen peroxide. The crystals then turn brown, but retain their form.

3. With nitric acid and potassium chlorate. Blackish brown flocks; on careful evaporation a strongly adhesive black-brown film of manganese peroxide, which may be rinsed off and tested as in 2, or before the blowpipe with soda. Limit of the reaction at 0.0002 m.grm. M. All the reactions described fall short of the above-named blowpipe reaction, which is at the same time exceedingly characteristic.

XI.—Cobalt.

1. With potassium nitrite and acetic acid yellow granules 2–4 micro.; from hot dilute solutions yellow cubes and octahedra 12–20 micro., and belonging to the compound $K_6CoN_{12}O_{24} + 3H_2O$. Valuable, as nothing but cobalt is precipitated, and the deposit adheres to the glass. Limit of the reaction at 0.0001 m.grm. Co.

In an ammoniacal solution no precipitate is produced by nitrite, but merely an intense yellowish brown colour. Acetic acid then occasions a precipitation. There is danger of confounding cobalt with nickel if calcium, strontium, or barium is present. (See Nickel 1).

2. With ammonium-mercury sulphocyanide. Splendid blue rhombs, mostly grown together in lumps and globes of peculiar form. With zinc and cadmium light blue mixed crystals. Limit of the reaction at 0.0003 m.grm. Co.

A solution of mercury sulphocyanide in a small excess of ammonium sulphocyanide is a good reagent in order to detect cobalt in presence of many other metals. With

* Zeit. Anal. Chemie.

nickel it gives no precipitate; with copper greenish rhombs and spears which appear *after* the blue crystals of cobalt. Hot water and also strong acids dissolve the crystals. Ammonia destroys the colour, which is restored by acetic acid.

3. With phosphor salt and ammonia. Crystals of the type of ammonium-magnesium phosphate, extended in length, and in presence of much sal-ammoniac and ammonia increasing to 100 micro. Limit of the reaction at 0.00002 m.grm. Co.

The precipitation is to be effected in the manner described under Manganese 2. The crystals are coloured brown by caustic soda and hydrogen peroxide. The blue crystals of reaction 1 are produced in their place by acetic acid and ammonium-mercury sulphocyanide. Nickel may be excluded as a preliminary by precipitating cobalt and manganese from an ammoniacal solution by means of hydrogen peroxide.

XII.—Nickel.

1. With potassium nitrite and lead acetate a yellow powder; from dilute solutions small yellow crystals of the triple salt, $\text{KNiPbN}_6\text{O}_{12}$, exactly similar to those of potassium cobalt nitrite. A quite similar but tardy reaction with barium, strontium, and calcium. Limit of the reaction at 0.000008 m.grm. Ni.

Potassium nitrite occasions no visible change in ammoniacal solutions of nickel. A granule of lead acetate occasions a deposition of pulverulent salts of lead. If acetic acid is then added, after gentle heating the yellow precipitate appears heaped up upon and around the salt of lead. It appears still instantaneously in the 6000 fold dilution of the nickel sulphate.

2. With phosphor salt and ammonia. Hemimorphous crystals, shorter than those of cobalt. They are not turned brown by caustic soda and hydrogen peroxide. Limit of the reaction at 0.00001 m.grm. Ni.

Precipitation with oxalic acid, proposed by Haushofer for distinguishing cobalt from nickel, cannot be recommended. For cobalt the limit of precipitation is at 0.00002 m.grm., but for nickel at 0.001. Cobalt oxalate falls rather sluggishly in the shape of fine needles and stars; nickel oxalate follows afterwards as a fine powder which renders the drop turbid. The ammoniacal solution of the oxalates displays a reversed behaviour on the evaporation of the ammonia. The nickel oxide falls after some time seemingly unchanged, whilst cobalt may remain in solution for hours in presence of much ammoniacal salt.

XIII.—Zinc.

1. With sodium bicarbonate. Colourless tetrahedra, 6–20 micro., of the compound $\text{Na}_6\text{Zn}_3\text{C}_{11}\text{O}_{35} + 8\text{H}_2\text{O}$, and crossed twin crystals of the same compound. Refracts light strongly, and adheres to the glass. Limit of the reaction 0.00001 m.grm. Zn. Limit of the immediate reaction at the 40,000 fold dilution of zinc sulphate.

From acid solutions sodium bicarbonate precipitates cadmium immediately in granules and zinc after about a minute in fine flocks. With an excess of alkaline carbonate there are gradually formed tetrahedra, whilst the liquid becomes clearer. With potassium and lithium the crystals are larger with predominating twin formation. Salts of ammonium, calcium, magnesium, and cadmium interfere. In ammoniacal solution there is immediate precipitation of cadmium, and no turbidity or formation of tetrahedra beginning at the margin. Magnesium interferes seriously, and must be previously removed by the cautious addition of phosphate.

2. With oxalic acid we obtain, even in presence of a considerable quantity of free hydrochloric acid, short prisms, generally rounded, of zinc oxalate,



of 20–25 micro. Easily soluble in ammonia. On its evaporation there are formed manifold ramified and curled rosettes of 200–700 micro. Cadmium interferes with their formation, and magnesium more so. In acid solu-

tions magnesium may cause the formation of a double oxalate in pale hexagonal tables of 40–60 micro. Sal-ammoniac opposes its formation. Limit of precipitation by oxalic acid 0.0001 m.grm. Zn.

3. With ammonium mercury sulphocyanide. From dilute solutions, and with a considerable excess of ammonium sulphocyanide, rectangular rods, otherwise forked and dendritic, often curiously curved and feathered. Magnesium has no influence. Cadmium slightly simplifies the formations. The colouration by cobalt (see Cobalt 2), may be used to detect zinc and cadmium in these precipitations. Limit of the reaction at 0.0001 m.grm. Zn.

4. With potassium ferricyanide. A yellow powder, but from very dilute liquids yellow cubes of 5–12 micro. Cadmium gives the same reaction. Limit at 0.00005 m.grm. Zn.

Zinc phosphate is easily soluble in ammonia, but does not form with it a crystalline double salt. On treating the arseniate in a similar manner we obtain crystals very similar to those of ammonium magnesium phosphate.

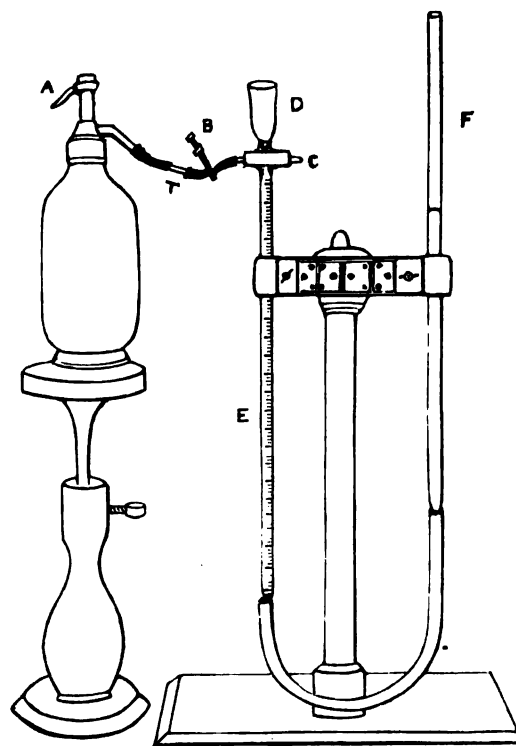
Zinc chromate resembles strontium chromate both in its appearance and in the conditions of its precipitation.

(To be continued).

AERATED MILK: DETERMINATION OF AIR.

By H. JOSHUA PHILLIPS, F.I.C. F.C.S.

MILK which has been deprived of its fat, and aerated with carbonic anhydride by Crampton's patent process, is now recommended by the medical profession for invalids whose digestive organs are incapable of assimilating raw milk.



The carbonic anhydride is forced into the separated milk contained in glass syphon bottles at a pressure of 80 lbs. per square inch, and from which quantities can be drawn as desired, the residual milk retaining its original flavour.

In order that the milk should keep for some time it becomes essential that the precipitation of the casein, &c., should be prevented by checking the propagation of lactic fermentation. In the course of some biological experiments the writer is instituting to this end, the determination of the amount of air present in the aerated milk became necessary, and the following is a sketch of the apparatus and details of the method employed. The tube T having first been filled with water to expel air, one end is fitted on to the end of the exit tube of the syphon bottle containing the milk, and the other to the three-way tube tap of Lunge's improved nitrometer previously filled with mercury. The tube T is supplied with a clip, B. The clip B having been relieved, the valve A is opened, when liquid and gas are forced into B. After about 40 c.c. of gas have been obtained, the valve A is dropped and the clip B closed. F is now lowered until the pressures are equalised. The temperature and pressure having been taken, the volume is read off. About 5 c.c. of a concentrated solution of caustic potash are now run into the funnel, D, and F lowered until the mercury is below the level of that in E; and by manipulating the stopcock, C, the liquid is made to run into E, the CO_2 is rapidly absorbed, and the air remains. After correcting for temperature and pressure its volume is obtained.

Stratford, London, E.

ON THE MOLECULAR WEIGHTS OF LIQUIDS AS EVINCED BY THEIR BOILING-POINTS.

By H. M. VERNON.

OF the methods for determining the molecular weights of bodies at present recognised, that depending on vapour density determinations can only give the molecular weight of a body when in the gaseous state, whilst those depending on Raoult's law of the molecular lowering of the freezing-point, on Van 't Hoff's law of osmotic pressure, and on the law of depression of the vapour pressure of a solution, only give the molecular weight of a body when dissolved in some solvent. Now, as the results obtained by Arrhenius, Ostwald, and others show that not only in some cases are the molecules existing in solution less complex in dilute than in concentrated solutions, but that these molecules frequently undergo a still further decomposition, and are split up into their free ions, which exist as such in the solution. It is therefore very probable that the molecules existing in a pure liquid undissolved in any other liquid, are in a more complex state of aggregation than when the liquid is so dissolved.

The object of this paper is to endeavour, by comparing volatile bodies as to some physical property, such as their boiling-points, to obtain some indication as to the probable value of their molecular weights when in the liquid state.

As a guide to the effect of molecular weight on the boiling-points of compounds, that afforded by certain well-known series of carbon compounds will at once be admitted. In these it is found that the addition of CH_2 to a compound generally raises the boiling-point about 19° , though the effect of introducing CH_2 into a compound already containing a considerable number of atoms of carbon is not so great as with a compound containing only a small number. Thus normal pentane and butane differ in boiling-point by 37° , undecane and decane by 22° , and nondecane and octdecane by 13° . Although the effect on the boiling-point of the introduction of CH_2 or other groupings into the molecule appears in many cases very simple, yet it must not be forgotten that in other cases this effect is greatly altered or even obliterated according to the structure the body formed takes up. An

idea as to the rise in boiling-point brought about by the doubling of the molecular weight of a body may be obtained from the behaviour of the members of the olefine series. Thus ethylene, C_2H_4 , boils at -105° , whilst butylene, C_4H_8 , boils at -5° . Octylene, C_8H_{16} , again, boils at 126° , and hexadecylene, $\text{C}_{16}\text{H}_{32}$, at 274° . Each doubling of the molecule is then attended with a rise in boiling-point of 100° or more.

It is proposed to first examine some of the principal inorganic liquids whose boiling-points are known, and to then study a few of the more important organic derivatives.

Of non-metallic inorganic compounds, one of the first that deserves notice is hydrofluoric acid. This body boils at 19.4° . Now hydriodic acid boils at about -25° , hydrobromic acid at -73° , and hydrochloric acid at about -100° . We should therefore expect hydrofluoric acid to boil at about -120° . The melting-points of these four bodies also vary in the same way. HI melts at -55° , HBr at -87° , HCl at -115° , and HF at about -40° . From vapour density determinations, Thorpe and Hambly have shown (*Chem. Soc. Journ.*, 1889, 163), that it is probable that the molecules of hydrofluoric acid at the boiling-point consist of H_4F_4 . This is about the value which we should arrive at from the abnormal value of the boiling-point, which we see is about 140° too high. From comparison with the members of the olefine series, we should expect a greater difference than this, but it is impossible to compare at all accurately such widely different bodies as these, so all the conclusions that can be drawn are that the molecules of liquid hydrofluoric acid have a molecular weight greater than that expressed by the formula H_2F_2 , and certainly not larger than H_4F_4 .

The next important exception is to be found in water. Its congener, sulphuretted hydrogen, boils at -61.8° , whilst even seleniuretted and telluretted hydrogen are gaseous at temperatures far below 0° . In order to arrive at a probable value of the boiling-point of water, supposing it to consist of simple H_2O molecules, we must compare some compounds of sulphur with the corresponding compounds of oxygen. There are, however, very few inorganic compounds fit for comparison, but such as are available show that sulphur compounds have considerably higher boiling-points. Thus SOCl_2 boils at 78° , but S_2Cl_2 , in which the atom of oxygen is replaced by one of sulphur, at 138° , or 50° higher. Chlorine monoxide, Cl_2O , boils at 19° , whilst Cl_2S boils, with decomposition however, at 64° , or 45° higher. Again, ozone boils at -120° , and SO_2 , which may be considered as derived from it by substitution of one atom of sulphur for one of oxygen, at -8° , or 99° higher. As will be shown later on, organic thiocompounds, with certain exceptions, boil at about 50° higher than the corresponding oxygen compounds. We may take it, therefore, that water, if consisting of simple H_2O molecules, would boil about 50° lower than H_2S , or at about -110° . It therefore boils some 210° too high. We have seen that in the case of hydrofluoric acid, an increase in boiling-point of about 140° indicates a molecular weight greater than $(\text{HF})_2$; water in the liquid state must therefore have at least the molecular weight expressed by the formula $(\text{H}_2\text{O})_4$. The author has shown (*Phil. Mag.*, May, 1891), that water, on being cooled to 4° , probably undergoes molecular aggregation, so the molecules below 4° probably have a molecular weight at least that expressed by the formula $(\text{H}_2\text{O})_8$. The fact that hydrogen peroxide, H_2O_2 , a body of nearly double the formula weight, does not solidify even at -30° , is additional support to the fact of liquid water having an abnormal molecular weight.

The next instances we come to are the oxides of chlorine. The monoxide, Cl_2O , boils at 19° , whilst the peroxide, ClO_2 , boils at 9° . Now such a substitution of an atom of oxygen for one of chlorine is in other cases attended with a slight fall in boiling-point. Thus SOCl_2 boils at 78° , and SO_2 at 46° , or 32° lower. The oxides of chlorine in the liquid state probably therefore have

molecular weights expressed by their ordinarily received formulae.

Elementary sulphur affords a marked exception. Its boiling-point is 448.4° , whilst oxygen, which in its compounds it so greatly resembles, boils at -182° . Selenium, which boils at 700° , and tellurium, which boils above this, must also have abnormal boiling-points. Thus bromine, whose atomic weight is more than double that of chlorine, boils at 63° , or only 97° higher than chlorine, whilst iodine boils at about 200° . Sulphur should therefore boil at about -90° , or at any rate very considerably below 0° . The fact that sulphur vapour just above its boiling-point consists of hexatomic molecules partly accounts for the high boiling-point, but even a treble molecular weight is not sufficient to explain a rise of over 500° . The molecules of liquid sulphur probably consist therefore of at least $(S_2)_6$ molecules, or molecules containing at least twelve atoms. This high value is confirmed by the fact of sulphur monochloride, S_2Cl_2 , boiling at 138° only, or 310° lower than sulphur itself.

The fact that SO_2 boils at -8° , and that $SOCl_2$ boils at 78° , whilst SO_3 , from which it may be considered as derived by substitution of two atoms of chlorine for two of oxygen, boils at 46° , shows that these bodies have normal molecular weights. Sulphuric acid, on the other hand is an exception, as it boils at 338° . Thus SO_2Cl_2 boils at 70° , and $SO_2 \begin{smallmatrix} Cl \\ OH \end{smallmatrix}$ at 158° , or 88° higher. Sulphuric acid, $SO_2(OH)_2$, should therefore boil at about 246° . Selenic acid also, which from its greater molecular weight would be expected to boil at a higher temperature, boils at about 280° , or 60° lower. Arguing from these data it is probably that the molecular weight is doubled, but it will be shown further on that it must be considered as having undergone a still further condensation, and that it consists in the liquid state of quadrupled molecules.

Selenium dioxide, SeO_2 , is the next exception. It boils at about 300° , whilst from the fact that its congener SO_2 boils at -8° , we should expect it to boil below 100° . Again, selenium oxychloride, $SeOCl_2$, boils at 179.5° . Now the analogous body, $SOCl_2$, boils at 78° , or 86° higher than SO_2 ; $COCl_2$ also boils at 8° , or 86.2° higher than CO_2 . SeO_2 we should therefore expect in a similar manner to boil some 86° lower than $SeOCl_2$, or at about 94° . The boiling-point of SeO_2 is thus some 200° too high. In the liquid state it must therefore consist of at least double molecules, and probably, from the conclusions arrived at in the analogous cases of HF and H_2O , of molecules of $(SeO_2)_4$.

The oxides of nitrogen showed no abnormalities in their boiling-points, except such as have long been accounted for by vapour density determinations. Thus the pentoxide boils at 45° , the tetroxide at 22° , the trioxide probably at a little below 0° , nitric oxide at below -100° , and nitrous oxide at -88° . The fact that the peroxide consists in the liquid state of N_2O_4 molecules is well shown by the boiling points, as if it consisted of NO_2 molecules it would boil at about -70° . Also it is evident that nitric oxide consists of NO molecules, for a liquid consisting of N_2O_2 molecules would boil at about -40° .

None of the halogen derivatives of phosphorus, arsenic, silicon, carbon, &c., appear to possess abnormal boiling-points, but they all show most striking regularity in in-

crease of boiling-point on substitution of bromine for chlorine in the molecules. The same regularity of boiling-point exists for such fluorides and iodides as are known. A few of the chief chlorine and bromine compounds are here given, and also the increase in boiling-point for each atom of bromine substituted.

This serves to show how regular is the increase in boiling-point with substitution of atoms of bromine in a molecule for chlorine. The irregularities mentioned above can therefore be no fanciful ones, due merely to the different arrangements of the atoms the molecules are made up of, but must be due to some more powerful influence, the existence of which can only be accounted for by supposing them to be due to differences of molecular weight.

Of metallic compounds little can be said, as so few of their boiling-points or even melting points are at all accurately known. It is possible nevertheless to find some well marked exceptions. Thus antimony trichloride boils at 216° , and is therefore probably normal, for this value is higher than the boiling-point of arsenic trichloride, which boils at 134° , to about the same extent as this value is higher than that for phosphorus trichloride, which boils at 76° . Its melting-point is, however, 76° , whilst that of the pentachloride is -6° . In the solid state, therefore, the molecules of the trichloride must have double the value of the pentachloride molecules. Stannous chloride also forms an exception, for it boils at a low red heat, whilst stannic chloride, $SnCl_4$, boils at 113.9° .

Now, to take as nearly similar a case as is available, C_2Cl_6 boils at 185.5° , whilst C_2Cl_4 boils at 121° , or 64.5° lower. If the body C_2Cl_8 existed, it would boil somewhat above C_2Cl_6 . $SnCl_4$ should therefore boil at about 80° lower than $SnCl_2$, or at about 40° . The molecules of liquid stannous chloride cannot therefore have a molecular weight smaller than that corresponding with the formula $(SnCl_2)_4$, and they probably have a considerably larger. The abnormal value for stannous chloride is rendered more evident when we consider that the bodies $TaCl_5$ and WCl_6 , with very high molecular weights, only boil at 241.6 and 346° respectively.

The fact that some halogen derivatives, as $SbCl_3$, $TiCl_4$, VCl_4 , &c., melt at temperatures below 0° , and that other derivatives, as $SbCl_5$, $SnCl_4$, CrO_2Cl_2 , $TiCl_4$, and $WOCl_4$, boil at temperatures not far removed from 200° , shows that some metallic compounds exist which, in the liquid state, have molecular weights expressed by their ordinarily received formulae, and are therefore strictly comparable with most non-metallic inorganic compounds. When, however, we examine the derivatives of most other metals we find a far different state of things to obtain. Thus the halogen derivatives of silver, thallium, and lead melt at about $400-500^{\circ}$, and boil at much higher temperatures, whilst if they consisted of simple molecules they should melt below 0° . Their molecules in the liquid state can thus scarcely consist of less than four or eight ordinary molecules. Again, the derivatives of the metals of the alkalis and alkaline earths only melt at about 700° , whilst their boiling-points are so high that they have not been determined; their molecules in the liquid state must therefore be still more complicated. What is true of these halogen derivatives may be applied equally to almost all the oxides and most other salts of the metals. Thus ruthenium and osmium tetroxides, chromium trioxide, and perhaps manganese heptoxide, are the only oxides which melt at temperatures below 200° , and of these OsO_4 and RuO_4 are the only ones which can be volatilised without decomposition. Most oxides do not even fuse at the highest temperature of the oxyhydrogen flame, so their molecules are in all probability exceedingly complex. Most other salts when exposed to high temperatures decompose without previous fusion, so it can only be concluded that their molecules are complex, without it being possible to say whether they are as complex as oxides.

The instances of abnormal boiling-points among carbon

Chloride.	Boiling-point.	Bromide.	Boiling-point.	Increase of b. pt. per each atom of bromine.
PCl_3 ..	76°	PBr_3 ..	175°	33°
$POCl_3$..	107.2	$POBr_3$..	195	29.3
$AsCl_3$..	134	$AsBr_3$..	220	28.7
BCl_3 ..	18.2	BBr_3 ..	90.5	24.1
$SiCl_4$..	59.6	$SiBr_4$..	154	23.6
$CHCl_3$..	61	$CHBr_3$..	151	30
CCl_4 ..	76.5	CBr_4 ..	189	28.1
CH_2Cl_2 ..	-22	CH_2Br_2 ..	4.5	26.5
$TiCl_4$..	136.1	$TiBr_4$..	230	23.5

compounds are very numerous, so only some of the more remarkable of them will be indicated here.

Hydrocyanic acid, boiling at 26.5° , form a well-marked exception. Thus cyanogen itself boils at -20.7° , or 47.2° lower, whilst the hydrogen derivatives of the halogens boil considerably lower than the analogously constituted halogens themselves. Thus chlorine boils at -34° , and hydrochloric acid boils at about -100° , or 66° lower. Bromine boils at 63° , and HBr at -73° , or 136° lower; iodine boils at about 200° , and HI at about -25° , or 225° lower. The effect of the introduction of hydrogen into the halogen molecule is thus less marked the more volatile the halogen. Now cyanogen is less volatile than chlorine, but considerably more so than bromine; it should therefore boil some 76° lower than its hydrogen derivative, or hydrocyanic acid should boil at about -96° . Its real boiling-point is thus some 122° too high. Now tricyanogen chloride, $C_2N_3Cl_3$, boils at 190° , whilst cyanogen chloride boils at 15.5° , or 174.5° lower; also paraldehyde boils at 124° , or 103.2° higher than acetaldehyde. We may therefore consider liquid hydrocyanic acid as probably the triple compound, especially as it is known that such triple molecules are of ready formation among cyanogen compounds.

It is a matter of doubt whether at temperatures just above their boiling-points aluminium methyl and ethyl have vapour densities corresponding to the formulæ Al_3Me_6 and Al_2Et_6 , or to half these formulæ. The boiling-points of these bodies indicate that in the liquid state the higher values obtain. Thus NEt_3 boils at 89° , and PEt_3 at 127° , or 38° higher; CMe_4 boils at 10° , and $SiMe_4$ at 30° , or 20° higher. Boron ethide, BEt_3 , boils at 95° ; aluminium ethide should therefore boil at about 125° , whilst in reality it boils at 194° , or 69° higher. Also boron methide boils at a temperature not far above 0° ; hence aluminium methide, boiling at 130° , has a value abnormal by a rather greater amount than for the ethide. It is evident, therefore, that in the liquid state the molecules of these bodies have the higher values.

We now come to more important exceptions, which, indeed, appear to extend to whole classes of compounds. Thus, from the study of boiling points it will be shown that in all probability all compounds, both organic and inorganic, containing one or more hydroxyl groupings, possess in the liquid state molecular weights double those expressed by their ordinarily received formulæ. Many of the derivatives of amidogen also appear to possess abnormal molecular weights.

To take firstly the organic hydroxyl derivatives, which consist principally of alcohols and acids. The reasons from which the conclusions as to their molecular weights are drawn are as follows:—

(1). The fact that all thio-compounds containing a sulphhydryl grouping boil some 30° or more lower than the corresponding hydroxyl compounds, whilst all other thio-compounds not containing a sulphhydryl grouping boil some 40° or 50° higher than the corresponding oxy-compounds, which also, of course, contain no hydroxyl groupings.

To prove the validity of this statement, most of the chief thio-compounds are here given, and also the number of degrees their boiling-points are above (+), or below (—), those of the corresponding oxygen compounds.

$(CH_3)_2S$..	+43°	CH_3SH ..	-46°	17.5°
$(C_2H_5)_2S$..	+56	C_2H_5SH ..	-42.3	56
$(C_3H_7)_2S$..	+48	C_3H_7SH ..	-29.4	64
$(C_4H_9)_2S$..	+55	C_4H_9SH ..	-6.5	50
$(C_6H_{13})_2S$..	+40	$C_6H_{13}SH$..	-15	124
$C_2H_5O.SEt$..	+38	$C_2H_5O.SH$..	-25	28
$CS.NEt$..	+73	$C_2H_4(SH)_2$..	-51.5	
$CSCl_2$..	+62			
$(CH_3)_4S$..	+49			

It would thus seem that, besides the thio-ethers having normal molecular weights, as is shown by the fact of their boiling-points being about 50° higher than those of the

corresponding oxygen ethers, the thio-alcohols also have normal molecular weights, and on this account boil at considerably lower temperatures than the corresponding oxygen alcohols, which exist as probably doubled molecules.

(2). The fact that most ethers, both simple and compound, in which the hydrogen of hydroxyl is replaced by a hydrocarbon grouping, boil at temperatures considerably below the boiling-points of the original hydroxyl derivatives, whilst in the case of thio-compounds the opposite is the case, the ethers boiling at temperatures considerably above those of the corresponding sulphhydryl derivatives from which they are derived.

In the last column in the above table are given the number of degrees the boiling-points of the thio-ethers are above the boiling-points of their corresponding thio-alcohols or acids. Here it will be noticed that in several cases the ethers boil at 50° or more higher than their corresponding alcohols, and that phenyl sulphide boils as much as 124° higher than thiophenol. The laws as to boiling-points are modified gradually as we pass from compounds containing a lesser to compounds containing a greater number of carbon atoms, so that with these the oxygen ethers begin to have higher boiling-points than their corresponding alcohols. Thus, phenyl ether, $(C_6H_5)_2O$, boils 69° higher than phenol. The difference between the boiling-points of phenyl sulphide and thiophenol is on this account much greater than the difference for compounds with a lesser number of carbon atoms. Nevertheless it is evident that phenol has a double molecular weight like other hydroxyl derivatives, as it boils higher than its corresponding thio-derivative in the same way that they do.

A few hydroxyl derivatives and their ethers are here given, together with their boiling-points. The last column gives the number of degrees the ethers boil below the hydroxyl derivatives.

Alcohol.	Boiling-point.	Ether.	Boiling-point.	Diff
$CH_3.OH$..	66°	$(CH_3)_2O$..	-23°	89°
$C_2H_5.OH$..	78.3	$(C_2H_5)_2O$..	35	43.3
$C_3H_7.OH$..	97.4	$(C_3H_7)_2O$..	86	11.4
$C_4H_9.OH$..	97	$(C_4H_9)_2O$..	85	12
$C_6H_{13}O.OH$..	118	$C_6H_{13}O.OC_2H_5$	77	41
$C_3H_7O.OH$..	140	$C_3H_7O.OC_3H_7$	122	18
$C_4H_7O.OH$..	163	$C_4H_7O.OC_4H_7$	157	6

Now it would be naturally expected that the substitution of a hydrocarbon grouping for an atom of hydrogen in any molecule would be attended by a rise of boiling-point, and such was seen to be the case with thio-compounds. Such, indeed, is the case with all compounds but hydroxyl derivatives. Thus the following instances show that the rise in boiling-point, on substitution of hydrogen by a hydrocarbon grouping, is considerable.

Substance.	Boiling-point.	Derivative.	Boiling-point.	Rise in boiling-pt.
$CH_3.CHO$..	20.8°	$CH_3.CO.CH_3$..	56.5°	35.7°
$CHCl_2.CHO$..	89	$CHCl_2.CO.CH_3$..	120	31
$C_2H_5.CHO$..	49	$C_2H_5.CO.CH_3$..	81	32
$C_6H_5.CHO$..	179	$C_6H_5.CO.CH_3$..	200	21
$C_6H_5.NH_2$..	183	$C_6H_5.NH.CH_3$..	191	8
$C_4H_4.O$..	35	$C_4H_3(CH_3).O$..	63	28
$C_4H_4.S$..	84	$C_4H_3(CH_3).S$..	113	29

How, therefore, can it be explained, except on the assumption of the doubling of the molecular weight of hydroxyl derivatives?

(3). Other groupings besides hydrocarbons, when substituted for the hydrogen of hydroxyl, also lower the boiling-point. Thus, for instance, compound ethers may be considered as alcohols with the hydrogen of hydroxyl replaced by an acid radicle. Now $C_2H_5.OH$ boils at 78.3° , but $C_2H_5O.CHO$, in which hydrogen is replaced by formyl, boils at 54.4° , or 22.1° lower; even the acetyl derivative, $C_2H_5O.C_2H_3O$, boils at 77° , or 1.3° lower.

When, however, the grouping formyl replaces a hydrogen atom in furfuran, the boiling-point is raised 127°. Again, ethyl nitrite, $C_2H_5O.NO$, boils at 16°, or 62·3° lower than ethyl alcohol; methyl nitrite boils at -12°, or 78° lower than methyl alcohol. Even methyl nitrate, $CH_3O.NO_2$, only boils at 66°, or the same temperature as methyl alcohol; whilst in other cases the substitution of $-NO_2$ in a molecule raises the boiling-point greatly. Thus benzene boils at 80·5°, and nitro-benzene at 205°. Again, methyl borate, $B(OCH_3)_3$, boils at 65°, or 1° lower than methyl alcohol, from which it can be considered as derived by substitution of $B(OCH_3)_2$ for its hydrogen atom.

Lastly, it is noticeable that some organic anhydrides—bodies which have nearly double the molecular weight of the free acids—boil at temperatures but slightly higher than those of these acids. Thus acetic anhydride boils at 137°, or only 19° higher than acetic acid itself.

(4). The complexity of the molecules of a few organic compounds at temperatures above their boiling-points has been proved experimentally by means of vapour density determinations. Thus both formic and acetic acids, at temperatures only slightly above their boiling-points, have molecular weights nearly three times those of their ordinarily received formulæ. It is not probable, however, that in most cases such molecular complexity extends to beyond the solid and liquid states.

(5). If some compound containing hydroxyl, as ethyl alcohol, be compared with other bodies of about the same boiling-point, and also containing an ethyl grouping, it will be rendered evident how very much greater is the molecular weight of these other groupings which go to form the molecule than is that of hydroxyl.

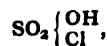
Substance.	Boiling-point.	Molecular weight.
$C_2H_5.OH$	78·3°	46
$C_2H_5.C_2H_5$	71	86
$C_2H_5.CHCl_2$	84	113
$C_2H_5.OC_2H_5$	66	86
$C_2H_5.N(C_2H_5)_2$	89	101
$C_2H_5.PH(C_2H_5)$	85	90
$C_2H_5.CH_2CHO$	75	72

These groupings, which from the boiling-points of the bodies produced by combining them with ethyl are comparable with hydroxyl, are, it is evident, quite incomparable from the standpoint of molecular weight. If, however, the molecule of liquid ethyl alcohol be supposed to have double the ordinary molecular weight,—namely, 92 instead of 46,—then it is of a value almost identical with the mean of the molecular weights of the bodies given, viz., 91. It is not, of course, even approximately correct to state that the boiling-point of a body depends only on its molecular weight; but it is scarcely possible that, of a series of bodies of about the same boiling-point, one should have half the molecular weight of any of the others, the molecular weights of all of these being of similar value.

If we examine again the thio-compounds, it will be seen that they also seem to indicate that hydroxyl compounds in the liquid state consist of double molecules, and are not in a higher state of complexity than this. Thus the thio-ethers boil at about 58° higher than the corresponding thio-alcohols. Oxygen ethers should therefore boil about this amount higher than alcohols, whereas they in reality boil about 40° lower. Alcohols, therefore, boil about 100° too high, which is about the increase found to obtain on doubling the molecular weights of the members of the olefine series. On calculating the boiling-points of other bodies as acetic acid in this manner, it is found that the calculated value, though considerably below the actual, is not nearly so much so as for alcohols. It may still be taken, however, to indicate the doubling of the molecule after the same manner as for alcohols; for it is a well-known fact that in many cases the increase of the molecular weight of a

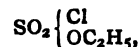
body by addition of other groupings is not attended by as great an increase of boiling-point if the body already has a high boiling-point as if it has a low one. Now acids boil some 40° higher than their corresponding alcohols,—so their boiling-points are accordingly not abnormal to so great an extent.

As regards inorganic hydroxyl derivatives, it is probable that they also in the liquid state exist as doubled molecules. There are not, however, so many data to prove this statement as there were for organic derivatives. Thus there are no sulphhydryl inorganic compounds to compare with the corresponding hydroxyl compounds, except sulphuretted hydrogen, which has been shown to be very much more volatile than water. Again, there are but two cases in which it is possible to compare the boiling-points of acids and the anhydrides from which they are derived. Nitric acid boils at 86°, and nitric anhydride at 45°, or 41° lower; whilst chlorsulphonic acid,—



boils at 158°, and disulphuryl chloride, $S_2O_2Cl_2$, at 146°, or 12° lower. Thus in each case the anhydride, though of nearly double formula weight, boils at a considerably lower temperature.

When the hydrogen of hydroxyl of such volatile acids as are known is replaced by a paraffin grouping, the boiling-point is lowered considerably. Thus dimethyl sulphuric ether, $SO_2(OCH_3)_2$, boils at 188°, or 150° lower than sulphuric acid; and the ethyl derivative boils at 208°, or 130° lower. Methyl nitrate boils at 66°, or 20° lower than nitric acid; ethyl nitrate boils at 86°, or the same temperature as the acid from which it is derived. Ethyl perchlorate, $C_2H_5ClO_4$, probably boils at a considerably lower temperature than perchloric acid. Ethyl chlorsulphonate,—



boils at 150°, or 8° lower than chlorsulphonic acid.

As, therefore, the above data show that hydroxyl containing acids in the liquid state have doubled molecular weights, chlorsulphonic acid must exist as a doubled molecule. Now it has previously been shown that the molecules of sulphuric acid are double as large as those of this acid; therefore in the liquid state sulphuric acid probably exists as quadrupled molecules.

Most organic derivatives containing amidogen, and many containing imidogen, groupings, appear to possess abnormal molecular weights, but they do not all seem to come under a general law in the same way as hydroxyl derivatives. All monamines and diamines—both primary, secondary, and tertiary—appear to possess normal molecular weights, and, on the other hand, many amidogen derivatives have molecules much more complex than merely doubled ones.

The existence of the amines as simple molecules is rendered evident by the fact of their boiling-points being slightly lower than those of the corresponding phosphorus compounds, whilst these are more volatile than the arsenic derivatives. Thus NH_2Et boils at 18°, and PH_2Et at 25°; NEt_3 boils at 89°, PEt_3 at 127°, and $AsEt_3$ at 140°. On comparing the amines with the corresponding halogen derivatives, it is found that a hydrocarbon grouping, combined with one or two amidogen groupings, has a boiling-point higher than the corresponding mono- or dichloro-derivatives, but lower than the bromo-derivatives. Thus $EtCl$ boils at 12·5° and $EtBr$ at 39°, $EtNH_2$ boiling at 18°. $C_2H_4Cl_2$ boils at 84° and $C_2H_4Br_2$ at 131°, whilst $C_2H_4(NH_2)_2$ boils at 123°. We have thus some sort of guide as to what the boiling-points of amidogen compounds should theoretically be by mere observation of the boiling-points of the corresponding halogen derivatives, for these have always been found to be normal. Acetyl chloride boils at 55°, the bromide at 81°; acetamide should therefore boil below 70°; in reality it boils at 222°,

or some 150° too high. Even diacetamide, $(C_2H_3O)_2NH$, only boils at about 212°. The acetamide molecule must accordingly, in the liquid state, be at least doubled, and probably trebled. The same arguments apply equally to the other amides of the fatty acids.

Glycocoll, $CH_2NH_2.COOH$, is not at all volatile, and indeed only melts at about 234°. The corresponding chlor- and brom-acetic acids, which, being hydroxyl derivatives, must have double molecular weights, boil at 186° and 208° respectively. The ethyl ester boils at 149°, and is therefore normal. These data show that the glycocoll molecule must be very complex, containing at least four, and probably more, ordinary molecules. The other amido acids and their derivatives are equally unvolatile, so their molecules must also be considered complex. Some of the derivatives of urea probably exist as doubled molecules. Thus the body $CO(NEt)_2$ boils at 212°, or considerably lower than $CO(NH_2)_2$, which boils at 263°. Succinimide boiling at 288° seems normal, as this value is but slightly higher than for succinic anhydride, which boils at 250°. Pyrrol, C_4H_4NH , however, appears to be abnormal, as it boils at 131°, whilst pyridine, C_5H_5N , only boils at 117°. Also the methyl derivative of pyrrol, $C_4H_4NCH_3$, boils at 113°, or 18° lower than pyrrol itself, whilst the isomeric derivative, $C_4H_3CH_3.NH$, boils at 148°, or 17° higher. It is therefore probable that pyrrol itself exists as a double molecule, but that the derivative, $C_4H_4.NCH_3$, which does not contain an imidogen grouping, exists as a simple molecule.

It seems probable that aniline has an abnormal molecular weight. Thus it has been shown that the phosphines boil higher than the amines, but the body $C_6H_5.PH_2$ boils at 160°, or 23° lower than aniline: also $(C_6H_5)_2PH$ boils at 280°, or 30° lower than $(C_6H_5)_2NH$. As $C_2H_5NH_2$ boils 7° lower than $C_2H_5PH_2$, aniline boils about 30° too high. Again, nitroethane, $C_2H_5NO_2$, boils 96° higher than ethylamine, so, as nitrobenzene boils at 205°, aniline should boil at about 109°, instead of 183°. Still again, monochlorobenzene boils at 132° and monobromobenzene at 155°, so aniline should boil at about 140°.

It will be seen that the subject of the molecular weights of amidogen derivatives is much more complicated than that of other classes of organic compounds. Only a few of the chief compounds have therefore been dwelt upon, as an exhaustive study of the whole class of these derivatives would be far beyond the limits of this paper.

We have thus seen that, by studying and comparing the boiling-points of compounds, it is possible, in a large number of cases, to determine with a considerable degree of probability the state in which the liquid molecules of these bodies exist. The subject has not been dealt with as thoroughly and exhaustively as it might have been; but the object of this paper was rather to indicate a method by which some sort of results might be obtained, so as to show that a careful study of the whole of the different classes of compounds, both organic and inorganic, with reference to their boiling-points, would not be without profit. The chief objection to the method is that the results obtained cannot be formulated with exactness, but can only be expressed in probabilities. It is likely, however, that with further study of the subject it will be possible to speak with greater certainty. Even if this is not so, the results may be considered to have a certain amount of value, as apparently no other method has yet been brought forward whereby the molecular weight of a liquid body, undissolved in any other liquid, is attempted to be determined.

Influence of Fluorides upon the Growth of Yeast.

—J. Effront.—Small additions of ammonium fluoride were found unfavourable to the increase of yeast, but gave nevertheless good results as regards the yield of alcohol.
—*Bull. de la Soc. Chim. de Paris*, v., No. 10.

INDIGO-GREEN: A COLOURING-MATTER OBTAINED FROM SULPHINDIGOTIC ACID.

By V. H. SOXHLET.

DURING the examination of various indigo extracts (indigo carmine, sodium sulphindigotate), to determine their market value, by a strange oversight a considerable quantity of liquid ammonia was poured into a glass containing indigo-carmine. The glass was stoppered, set aside, and left to itself. After about ten days it was again taken up, when, on the point of having it cleared out, I perceived that the colour of the liquid had changed from a deep blue to a yellowish green. This was the origin of the present communication.

On a superficial examination of the yellowish green liquid, it appeared that several colouring-matters must be present, for, although of a very intense yellow, if slightly sprinkled upon white filter-paper, it showed shades varying from the deepest dark blue to the palest straw-yellow. Hence it was doubtful if the observation could be made available for practical purposes. The only similar substance which I found described was the sulphoviridic acid of Berzelius. This compound was obtained by evaporating to dryness a solution of barium sulphindigotate, precipitating the re-dissolved barium salt with basic lead acetate, and decomposing with sulphuretted hydrogen. Sulphoviridic acid, however, though it is a green dye-ware, is soluble only in absolute alcohol, and has consequently met with no technical application.

I began my experiments in a regular manner, weighing out equal parts of indigo extract, and mixing them with liquid ammonia (sp. gr. 0.936) in increasing proportions, as 1:1, 1:2, 1:3, and 1:5, stopping the glasses well and letting them stand for eight to ten days.

On examination at the end of this time it appeared that the specimens which had received the largest additions of ammonia displayed the finest green colours, whilst specimens which had been mixed only with equal or double weights of ammonia showed a dark bluish green. We may assume that, even on using only equal parts of indigo-carmine and ammonia, corresponding results would be obtained if the action were sufficiently prolonged. It is easy to understand that the acidity of the indigo-carmine, or the indigo extract, will play here an important part.

It was not to be expected that the green dye-ware, in its alkaline state, would be able to dye wool, as I soon convinced myself by a small experiment. One specimen of the green solution of indigo was mixed with dilute sulphuric acid until the mixture had a faintly acid reaction. I then added a solution of sodium chloride of the strength of 14° Tw., stirred it up well, and filtered it through felt. The feebly acid filtrate had a light green colour, but was red by reflected light—a further analogy with the sulphoviridic acid of Berzelius. The paste obtained had the appearance of commercial indigo-carmine, but without its coppery lustre. It was easily soluble in warm water. White yarns took on, in the hot solution, a shade closely resembling that of methyl-green, and which retains the green colour by gas- or candle-light.

The operation of dyeing went on normally; the colour took upon the fibre more evenly than indigo preparations do; the fastness against light is equal to that of indigo extracts. Its fastness against washing, alkalis, &c., is decidedly better. Experiments on the large scale have not yet been made with this dye, as I wish to determine the method of manufacture more precisely.

In experiments on preparing the indigo-green on a larger scale I used the commercial dry extract, such as it is chiefly made and used in England. It has certain advantages as compared with the paste, since it is more easily mixed with the ammonia, and generally contains less free acid than the semi-fluid paste.

On more prolonged action of ammonia upon indigo

extra $\dot{c}$ no essential difference could be detected in the dyed shades, though the original ammoniacal liquid had decidedly a more yellow colour. Even when the ammoniacal solution of indigo had become a yellowish brown, on neutralising it with sulphuric acid a green was always obtained on the fibres.

Further experiments, to treat potassium sulphindigotate with ammonium carbonate under pressure had a negative result. If a solution of indigo extra $\dot{c}$ is treated with liquid ammonia and caustic soda-lye a yellow colouration rapidly appears. But this product will scarcely admit of practical applications, as it dyes up only dirty shades on wool and silk.

The author's indigo-green consists at least of two colouring-matters, which dye respectively yellow and green.—*Chemiker Zeitung*.

NOTICES OF BOOKS.

The Organic Elements and their Position in the System.

An Address delivered before the German Chemical Society at Berlin, on March 23rd, 1891. (*Die Organischen Elemente und ihre Stellung im System. Ein Vortrag gehalten in der Deutschen Chemischen Gesellschaft zu Berlin, am 23ten Maerz, 1891*). By W. PREYER. Wiesbaden: J. F. Bergmann (8vo., pp. 47).

PROF. PREYER undertakes here an arduous and a twofold task. He seeks, as do not a few of the more philosophical men of science of the day, to introduce the concept of evolution into general chemistry, though he admits it will only attain recognition after a long time. He at the same time raises the difficult question why only certain elements, to the exclusion of others, play a necessary part in the maintenance of life upon our earth? As such he acknowledges only fourteen, all of which have atomic weights lower than 56. His organic elements are hydrogen, carbon, nitrogen (which our French neighbours ought to have called "zote" instead of azote), oxygen, fluorine, sodium, magnesium, silicon, phosphorus, sulphur, chlorine, potassium, calcium, and iron. Here, already, there is room for discussion. How are we to exclude copper from the list? It is found in vegetable products of various kinds, grown upon the soils of different geological formations, and more especially in the cacao-nut. We do not mean in the cocoa or chocolate of commerce, where it might possibly have been introduced by the instruments or ingredients used in the manufacture, but in the nuts as plucked from the tree.

There are cases in which copper appears to be not merely absorbed by animals, but assimilated. Harlen detected copper in the blood and in the liver of certain mollusks, especially cephalopods. His experiments indicate that in them this element "stands in an essential relation to the blood-corpuscles." In the blood of the cephalopods there has been detected an organic copper compound, known as hæmocyanine, which fulfils the functions due in the higher animals to hæmoglobine.

Von Bibra detected copper in certain crustaceans, such as *Cancer pagurus*, and found that it occurred in an inverse ratio to the iron, which it more or less completely replaced. Dr. Genth quantitatively determined the copper in the blood of the *Limulus*, a crab found on the coasts of North America. The blood of the healthy females, just before laying their eggs, was of a rich blue, and when dried the incinerated residue contained 0.295 per cent of copper oxide and but a mere trace of iron oxide. Surely these observations should be proved erroneous before copper is deleted from the list of organic elements.

In like manner Prof. Preyer thinks it "not improbable that those oceanic plants and animals in which iodine and bromine are regularly found would flourish as well in waters in which these elements are wanting." The only answer to this question is experimental. If anyone can

find plants or animals of the same species which otherwise contain iodine or bromine, living and increasing in the absence of these halogens, the author's argument—which is merely an assertion of non-improbability—holds good. But until such *à posteriori* evidence is produced it cannot be accepted.

The argument that the number of organic elements cannot exceed fourteen, because the milk of the highest animals contains no more, is not trustworthy. We have no proof that additional elements are not present in the Articulata, in the Mollusca, or in plants. Iodine, bromine, copper, may be eliminated in the progress of higher development.

Prof. Preyer, in concert with Dr. Wendt, endeavours to lay down, *à priori*, the number of possible elements of which our earth—or rather its upper strata—may consist. He holds that their number must be at the utmost 91, and at the lowest 84, of which 68 are already known. Here, again, we should prefer to leave the question open, and await the results of spectroscopic and micro-chemical analysis.

But whilst a certain portion of Prof. Preyer's researches must, for the present at least, be entered in a "suspense account," his labours in extending the great principle of evolution to the chemical elements deserve the fullest recognition. We find here a quotation from Prof. Kekulé which has not received the attention it merits:—"The relations of a body to that which it once was, and to that which it may become, form the essential object of chemistry."

The late regretted Clemens Winkler—too early lost to Science—declared his conviction that the chemical elements have arisen from "more simple matter," "from a primal matter" (protyle), "unknown to us and engaged in a gradually progressing condensation."

If the chemical elements have neither been created nor developed from some primary material,—both which origins Prof. Mendeleeff denies,—how can we possibly account for the relations which exist between them? Such relations seem to us absolutely unthinkable among a set of bodies which have come into existence at haphazard, or equally by chance have existed in the universe from all eternity.

CORRESPONDENCE.

A CASE OF META-CHEMISTRY.

To the Editor of the Chemical News.

SIR,—In a paper on "Destructive Distillation" which Dr. Mills has published in the June number of the *Journal of the Society of Chemical Industry*, he brings forth fresh evidence in favour of his pet theory (see same Journal, year 1885, p. 325) that, in things like coal, shale, &c., "the distribution of the original material is based upon a C_3 unit."

A Scottish bituminous coal, bearing the jaw-breaking name of "Balquhatstone," was analysed and found to contain—

Carbon	82.54	} 93.00
Hydrogen	4.88	
Oxygen	5.58	
"Pit Water" ..	2.52	
Nitrogen	1.75	
Sulphur	0.77	
Ash	1.96	

100.00

From these numbers Dr. Mills concludes that the "carbon, hydrogen, and oxygen have the relation $C_{18}H_{12}O$," and then, referring to his book on "Destructive

tive Distillation" (pp. 39, 40, 56), compares this formula with others similarly worked out:—

Yorkshire and Durham	$C_{24}H_{18}O$
Balquhatstone	$C_{18}H_{12}O$
Boghead	$C_{12}H_{10}O$
Average Cannel	$C_{12}H_{12}O$
Heywood Gas Cannel	$C_9H_{12}O$
Good average Scotch Shale ..	$C_6H_{10}O$

But what do these formulæ prove? Why, any person who, besides being a chemist (I mean one of the orthodox at least of the para-kind), is not utterly devoid of the faculty of arithmetical reasoning, will simply laugh at these meta-chemical exercises. In the present case, indeed, the results of the analysis agree far better with the formula $C_{20}H_{14}O$ than with Dr. Mills's own, as seen by the following comparative statement:—

	Found.	Demanded by	
		$C_{18}H_{12}O$	$C_{20}H_{14}O$
Carbon	88.76	88.53	88.89
Hydrogen	5.25	4.91	5.19
Oxygen	6.00	6.56	5.92
	100.00	100.00	100.00

In a similar manner small-integer formulæ, not "based upon a C_3 unit," might be calculated for the Yorkshire, Boghead, Average Cannel, &c., but it is not worth while to do so; I prefer to confidently give it as my opinion that all Dr. Mills's formulæ—inasmuch as they pretend to do more than symbolise the direct results of the respective analyses—are just meta-chemistry pure and unmixed, or, to put it into plainer English, unmitigated ———. The same remark is a sufficient critique of Dr. Mills's monstrous equations to explain the re-distribution of carbon, &c., which takes place when that "Balquhatstone" (I hope I have spelled it correctly) is subjected to dry distillation at low temperatures and high temperatures respectively. For the benefit of those of your readers, however, who have not the *Soc. Chem. Ind. Journal* at hand, I will reproduce the low-temperature equation as a specimen:—



In a similar manner one might, in reference to the cooking of a steak, formulate the relation between the several portions of carbon, hydrogen, and oxygen which pass into the cooked steak, the gravy, and the chimney respectively! And thereby render an additional service to—Meta-Chemistry.—I write in the name of

COMMON SENSE.

July 25, 1891.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—I was a competitor in the recent examination of candidates for the Associateship of the Institute of Chemistry. The general arrangements gave great dissatisfaction to the majority of the examinees, and I am curious to learn if members of the Institute consider an examination so conducted a test of the capabilities of the competitors.

At the London centre fifteen candidates presented themselves. Three balances only were provided, and one of these was in bad working order; the balance cases were devoid of drying material, and no proper weighing tubes or watch-glasses were obtainable. There was but one sulphuretted hydrogen Kipp in the laboratory, and no solution of the gas. The benches were unprovided with most necessary reagents, and even the concentrated mineral acids had to be taken as required from large stock bottles at one end of the room. The utensils and apparatus provided were quite inadequate for the proper performance of the work set, and candidates were com-

pelled in consequence to resort to obsolete and unreliable methods.

I am convinced that no one could obtain reliable results under such conditions, and that it would be practically impossible to discriminate between the good and bad workers. It seems probable that inferior men may be admitted as Associates in consequence, and possibly good men rejected. I should like to know from any of your readers if this examination is generally regarded as a fair test, and if so, whether it has not this year degenerated from the usual standard.—I am, &c.,

ZERO.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 2, July 13, 1891.

A Contribution to the Study of so-called "Natural Meadows."—A. Chatin.—The author defines natural meadows as those composed chiefly of plants belonging to the family of the Gramineæ, whilst artificial meadows are composed of leguminous plants, lucerne, clovers, sainfoin, and medicago.

On the Cyanalkoylic, Cyanobenzoyleic, and Cyanorthotoluylic Camphors.—A. Haller.—The author's researches prove that camphor contains a group—



as Kekulé's formula requires. A further proof of the presence of this arrangement of atoms is the property which camphor possesses of giving rise to the isonitro-camphor of Claisen and Manasse.

On a New Copper Hydride and on the Preparation of Pure Nitrogen.—A. Leduc.—The new compound has nothing in common with the compound discovered by Wurtz, which is formed in the cold and destroyed entirely about 60°. Leduc's hydride is produced at a dull red heat by the direct union of its elements, and presents mere traces of dissociation at a cherry-red heat. It is a body of a fine hyacinth red, which covers the metal. It appears certain that the hydrogen is really combined with and not dissolved in the metal. The author considers it interesting to resume the study of the decomposition of gaseous ammonia by metals and especially by copper.

Action of Light upon Silver Chloride.—M. Guntz.

—On exposing $AgCl$ to light in a thin layer upon a plate of glass, it is in the first moments only coloured very slightly, but if it is then placed in the solution of iron oxalate the silver chloride is reduced, with a formation of metallic silver. Even in the absence of light the author has succeeded in producing a modification of silver chloride which is directly reduced by the oxalate solution. To obtain this modification it is merely necessary to boil silver chloride for some hours in the absence of light. If, on the contrary, silver chloride is left for some time exposed to the light it takes a violet-red tint and loses chlorine. The silver sub-chloride formed on prolonged exposure to light yields, on further reduction, metallic silver. A layer of silver chloride after exposure to light consists of three superimposed layers, metallic silver, silver subchloride, and unaltered $AgCl$.

On a New Gaseous Compound: Phosphorus Pentafluorochloride.—C. Poulenc.—The compound in question, PF_5Cl_2 , is a colourless gas, possessing an irritating odour, not combustible in the air, and instantly

absorbed, with decomposition by boiled water. Alkaline solutions, lime-water, and baryta-water, absorb it. Its density, as determined by Chancel's apparatus, is 5.40, the theoretical density being 5.46. At common pressures it is liquefied at a temperature bordering upon -80° . At 250° it is decomposed, yielding gaseous phosphorus pentafluoride and solid phosphorous pentachloride. At 115° sulphur reacts upon phosphorus pentafluorochloride, yielding sulphur chloride and a new gaseous compound, phosphorus sulphofluoride. This gas has a peculiar offensive odour, it is rapidly absorbed by an alkaline solution, and is split up in contact with water, yielding hydrofluoric acid, phosphoric acid, and hydrogen sulphide. Ammonia combines at common temperatures with phosphorus pentafluorochloride, forming fluorophosphamide—a white, light solid, soluble in water.

Combination of Boron Bromide with Hydrogen Phosphide. Boron Phosphide.—A. Besson.—Boron bromide absorbs hydrogen phosphide at common temperatures, forming a very light amorphous solid, which fumes and ignites spontaneously on exposure to the air. It can be examined only in an atmosphere of carbon dioxide perfectly dry. Its composition is shown by the formula BBr_2PH_3 . Boron phosphide, PB, is a brown solid, insoluble in water, soluble in concentrated boiling alkalis, with formation of hydrogen phosphide. Monohydrated nitric acid decomposes it with brisk incandescence; dilute nitric acid decomposes it violently. It burns in the cold if thrown into chlorine gas.

Researches on the Alkaline Earthy Zirconates.—L. Ouvrard.—The author has obtained the calcium, strontium, and barium zirconates. His researches establish an additional analogy between zirconium, tin, and titanium.

Artificial Production of Datholite.—A. de Gramont.—This paper does not present any chemical interest.

Action of Boron Fluoride on the Nitriles.—G. Patein.—Boron fluoride combines in definite proportions, molecule to molecule, with the nitriles both of the fatty and the aromatic series.

On the Acid Sulphated Ferrugino-Aluminic Waters of the District of Rennes-les-Bains (Arde).—Ed. Willm.—This memoir, though placed under the heading "analytical chemistry," does not describe any new or improved analytical process, but merely gives the composition of certain mineral waters.

On the Formation and Oxidation of Nitriles during Nitrification.—S. Winogradski.—In a number of experiments made with soils from different countries, nitrification always began with the formation of nitrous acid, which rapidly increases in quantity. When the ammonia present in the "culture" had disappeared, the nitrite formed was oxidised and very rapidly converted into nitrate. The exotic nitric ferments isolated were without action upon ammonia.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. v., No. 10.

On Levosine, a New Proximate Principle of some Cereals.—C. Tanret.—Anhydrous levosine may be represented by the formula $\text{C}_4\text{H}_{40}\text{O}_{40}$. It is a white amorphous body, almost tasteless. It is very soluble in water in all proportions, and dissolves freely in weak alcohol, but scarcely in alcohol at 95° . It does not reduce Fehling's liquid, and does not ferment with beer-yeast. Diastase—whether obtained from malt, from bran, or from saliva—has no action upon levosine.

On a Crystalline Compound of Absolute Alcohol and Sodium Disulphide.—L. Dumont.—The compound in question has the composition $\text{C}_4\text{H}_6\text{O}_2 + 9(\text{NaS}_2)$. If placed in a dry desiccator, at the ordinary pressure, it is converted into a mixture of sodium thi. sulphite and sulphite and a little sulphur.

Action of Benzyl Chloride upon Orthotoluidin.—Ch. Rabaut.—The product of this reaction is an oil of a pale yellow colour, which appears to be benzyl orthotoluidin, and is composed of 84.49 per cent carbon, 8.02 of hydrogen, and 7.48 nitrogen.

Determination of Acetone in Denaturated Alcohols.—Leo Vignon.—The determination of acetone is effected by utilising Lieben's reaction, which consists in transforming acetone into iodiform by the simultaneous action of iodine and soda. The author operates in the following manner:—After having sought for aldehyd, and eliminated it if needful, according to the indications of Barty, he takes 5 c.c., which are made up to 250 c.c. with distilled water (A). In a test-glass having a foot, graduated to 100 c.c. and fitted with a ground stopper, he introduces 10 c.c. of binormal soda [2NaOH in grms. = 1 litre] and 5 c.c. of the mixture A. After shaking up there are poured into the glass 5 c.c. of binormal iodine [$2\text{I} + 2\text{KI}$ in grms. = 1 litre], and the whole is shaken up again; the iodine liberated is dissolved by the addition of 5 c.c. of ether. On weighing the residue from the evaporation of 5 c.c. of ether, under known conditions, the quantity of acetone is known. But the result must never be accepted as final until it is confirmed by a determination effected with a double quantity of iodine and soda.

Pump which is Automatically Re-filled with Mercury by means of the Water Pump.—A. Verneuil.—This paper requires the accompanying figure.

Composition of the Brandies and Alcohols of Commerce.—Ed. Mohler.—The author expresses the acids as acetic acid, after determination with decinormal potassa. The ethers are expressed as ethyl acetate, and determined by saponification with decinormal potassa. The aldehyds are expressed as ethylic aldehyd, and determined colorimetrically after treatment with rosaniline bisulphite by comparison with a type-solution of aldehyd at 1-20,000. The higher alcohols are expressed as isobutylic alcohol (or amylic alcohol in case of industrial alcohols), and determined by the colour reaction of sulphuric acid upon alcohol freed from aldehyds by means of aniline diphosphate and a colorimetric comparison with a type solution of amylic or isobutylic alcohol at 1-5000. The nitrogenous products are estimated as ammonia.

Remarks on the Phenomenon of Coagulation: Fibrine and the Coagulation of the Blood.—A. Béchamp.—The author absolutely distinguishes between the coagulation of milk and that of blood. He maintains that fibrine is not a proximate principle, but a mixture formed by a special albumenoid matter inclosing microzymes of a peculiar kind.

Reply to M. Le Bel concerning the Criticism of the foregoing Communication.—A. Béchamp.—A controversial paper, for which we must refer to the original.

Action of Hydroxylamine upon the Acetonic Nitriles.—M. Hanriot.—Not suitable for abridgment.

Vol. v., No. 12.

The Basic Magnesium and Zinc Chromites, and Neutral Cadmium Chromite.—G. Viard.—The object of the present research is to show that magnesium and zinc can yield basic chromites, whilst cadmium under the same circumstances only yields a neutral chromite.

On Turpentine.—Raoul Varet.—Aluminium chloride polymerises the essential oil of turpentine, whilst there is at the same time a formation of cymene, colophene, and other carbides, though in smaller quantities. Turpentine, under the influence of bromine and aluminium chloride, is not split up into isopropyl bromide and a bromo-derivative of toluene.

The Use of the Calorimetric Bomb for Determining the Combustion-heat of Coal.—Scheurer-Kestner.—The use of the calorimetric bomb has constantly yielded lower results than those of the old

calorimeter of Favre and Silbermann. The differences generally lie between 100 and 200 calories. The author thinks that the bomb is more trustworthy, and that its indications should be preferred.

Journal für Praktische Chemie.
New Series, Vol. xliii., Parts 9 and 10.

On the Naphthoic Acids.—A. G. Ekstrand. (Conclusion).—Experiments on nitration with β -naphthoic acid have very complicated results, since there are formed several—probably five—mononitro-acids, the separation of which is by no means perfect. In the β -naphthoic acid, as in the corresponding α -compound, the nitro-group is found introduced by preference into the α -position of the benzene nucleus. The nitro- β -naphthoic acids are very similar in their constitution and their properties. The remaining three mononitro-derivatives are formed only in subordinate quantities.

Researches from the Laboratory of A. Weddige.—These comprise a memoir by E. Zacharias on the action of ammonia upon substituted ortho-amido-benzoic ether, and a paper by V. P. Thieme on the action of ammonia and methylamine upon nitrised oxybenzoic ether.

Researches from the Laboratory of the University of Freiburg.—The continuation (Section lxxxvi.) of a treatise on ortho-para-dinitrophenyl and nitroazo- or nitro-nitrosoazo-para chlorophenyl hydrazin and their derivatives.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vi., No. 63.

This issue does not contain any chemical matter.

Vol. vi., No. 65.

Industrial Production of Lactic Acid.—Georges Jacquemin.—The author prepares a saccharine fermentable wort from malt, introduces pure lactic ferment produced by the method of Pasteur, as also a quantity of pure, sterilised calcium carbonate, and allows the mixture to ferment at 40° to 45°. The fermentation lasts five or six days. The fermented liquid is filtered and evaporated, when an inodorous calcium lactate crystallises out.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xiv., No. 4.

This issue contains no chemical papers.

MISCELLANEOUS.

British Institute of Preventive Medicine.—Sir Michael Hicks-Beach, who previously gave a negative answer to the request made by the Executive Committee of the British Institute of Preventive Medicine, having reconsidered his decision, has now granted the required license to register the Institution as a Limited Liability Company, with the omission of the word "Limited." The license, however, is not to be construed as expressing approval by the President of the Board of Trade of experiments on animals, or in any way effecting the exercise by the Secretary of State of his discretionary powers to grant a vivisection license to the proposed Institute. The articles of association have been signed, and the Institute is now duly registered. The following gentlemen have already expressed their willingness to serve on the Council:—Sir Joseph Lister (Chairman), Sir Charles A. Cameron, Mr. Watson Cheyne, Prof. Michael Foster, Prof. Greenfield, Prof. Victor Horsley, Sir Wm. Roberts, Sir Henry Roscoe, Prof. Roy, Prof. Burdon Sanderson, Dr. Pye-Smith, and Dr. Armand Kuffer, of 19, Iddesleigh Mansions, Westminster, S.W., will act as hon. sec. until the first meeting of the Council.—19, Iddesleigh Mansions, Westminster, July 29, 1891.

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NOTICE IS HEREBY GIVEN, that

CECELIA STEPHAN and RICHARD SOUTHERTON, both of 9, Chandos Road, Highbury Park, Birmingham, Co. Warwick, have applied for leave to amend the specification of the Letters Patent, No. 10,266, of 1888, granted to JOHN ALFRED STEPHAN and RICHARD SOUTHERTON for "Improvements in the Manufacture of Aluminium and its Alloys."

Particulars of the proposed amendment were set forth in the "Illustrated Official Journal (Patents)," issued on the 8th July, 1891. Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one calendar month from the date of the said Journal.

(Signed)

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THE CHEMICAL NEWS.

VOL. LXIV., No. 1654

THE CONSTITUTION OF THE LIGNO-CELLULOSES.

By C. F. CROSS and E. J. BEVAN.

I.—Recent Investigations of Soluble Products of Wood Boiling (Bisulphite Cellulose Process).

THROUGH the kindness of our friend Prof. Tollens, we have received an early copy of the *Inaugural Dissertation* (Gottingen, 1891), of J. B. Lindsey, embodying the results of an extended investigation of the products of the now widely-known "bisulphite" process of treating wood for converting it into a paper-maker's pulp (cellulose). The object of the author, working under the guidance of Prof. Tollens, was to throw light on the constitution of the substance of fir-wood, and the results obtained appear to us to deserve to be promoted without delay from the academic atmosphere in which they first see the light to the "open air" of "working chemistry." We will therefore give a brief abstract of these results, noting subsequently the points in which the author has been able to develop the main subject of his inquiry, viz., the constitution of the lignone, or *non-cellulose* constituent of the wood substance (ligno-cellulose).

This is converted by the process of digestion (at 108° C.—Mitacherlich process) into a soluble derivative, probably, as the author premises, with the minimum of change, and the first part of the work is therefore devoted to the investigation of the waste liquors of this process, holding in solution 9—10 per cent of "total solids." Of these the inorganic constituents are mainly calcium sulphate and sulphite. In the organic constituents the author found small quantities of pentaglucofoses, probably xylose, and of galactose or galactan, traces of vanillin, and some quantity of mannose. But by far the larger proportion, say 90—95 per cent, the author finds to be made up of the amorphous or gummy solid which characterises the residue of evaporation. This compound was isolated in a variety of forms, showing a satisfactory uniformity in empirical composition. Of these we may cite the following, omitting the details of the preliminary purification:—

- | | |
|--|--|
| (a) Precipitated by alcohol. . . | $C_{24}H_{24}(CH_3)_2SO_{12}$ |
| (b) Gums precipitated as lead compounds. { | (1) $C_{24}H_{24}(CH_3)_2SO_{12}$ |
| | (2) $C_{24}H_{24}(CH_3)_2SO_{12} \cdot 1\frac{1}{2}H_2O$ |
| (c) Precipitated by HCl . . . | $C_{24}H_{24}(CH_3)_2SO_{10}$ |
| (d) Precipitated by Br. . . . | $C_{24}H_{22}(CH_3)_2Br_4SO_{11}$ |

These bodies may be regarded as derived from the compound $C_{24}H_{24}(CH_3)_2O_{12}$, which is therefore well established, subject to the conditions premised, as *the empirical formula for the lignone constituent of fir-wood*.

The insoluble product of the manufacturing process, i.e., sulphite cellulose, was found to be partially converted into dextrose by treatment with concentrated sulphuric acid. By the action of strong nitric acid this cellulose, and also the original wood, was converted into an oxycellulose, having the empirical composition:—

C	..	..	..	43.41
H	..	..	..	6.19
O	..	..	..	50.40

Similar therefore in composition, as it was found to be

in its properties, with that obtained by ourselves from cotton (*Chem. Soc. Jour.*, 1883).

Such is a brief outline of the author's results, and upon them we offer one or two comments.

The empirical formula deduced by ourselves for the lignone constituent of jute, from the study of its chlorination products (*Chem. Soc. Jour.*, 1889, 213), was $C_{76}H_{80}O_{37}$, which differs but little from Lindsey's formula (*supra*) for the non-cellulose of firwood; for $3 \times C_{26}H_{30}O_{12} = C_{78}H_{90}O_{36}$.

The proportion of methyl groups in the above formula was determined by the hydriodic acid method; they are therefore present as $O \cdot CH_3$ groups. In our paper on the "Constitution of the Jute Fibre Substance" (*loc. cit.*), we noted the formation of acetic acid by the solution of the fibre in sulphuric acid, and deduced from the observation that the CH_3 groups were in union with CO groups. Both conclusions may be true, and would appear to be justified by the study of the products of destructive distillation, of which both $CH_3 \cdot CO$ and $O \cdot CH_3$ groups are prominently characteristic.*

The author does not appear to have attempted to diagnose the mode of union of the S atom in the molecule of the derivative of the lignone. It is important, however, to have established the fact of its presence in combination; and it will no doubt prove to have an important bearing on the theory of this process of cellulose isolation. We are engaged, on the other hand, in studying the derivative obtained in the sulphurous acid (Pictet) process of resolving pine-wood, which is of an obviously simpler character, and appears to yield a derivative more closely related to the original lignone than that investigated by Lindsey and Tollens.

Lastly we note that the authors retain the term *lignin* for the non-cellulose constituent of the ligno cellulose; seeing that the characteristics of the body are those of a ketone, we have suggested the substitution of the term *lignone*, which we think preferable.

II.—Oxidation of Ligno-Celluloses by Chromic Acid.

In our earlier contributions to the chemistry of cellulose (*CHEMICAL NEWS*, xlii., 77; *Chem. Soc. Jour.*, xxxviii., 666) we noticed that the cellulose, isolated by the chlorination method was not homogeneous, containing a form of cellulose easily hydrolysed by acids and alkalis to soluble derivatives; further, that by suppressing or limiting as far as possible the conditions tending to hydrolysis in the process of separating the cellulose, the proportion obtainable, i.e., percentage yield on the raw fibre, could be considerably increased.

Thus, by preventing the rise of temperature in chlorination, and digesting subsequently in aqueous sulphurous acid at 0°, the yield was increased to 80—82 per cent from the 74—76 per cent obtainable without these precautions.

These observations led us to the conclusion—which we give in the words of our first paper (1880)—that "as the cellulose is not homogeneous, and the percentage yield varies with the several methods by which the inter-cellular substances may be removed, we have reason for believing them to contain a body allied to cellulose. The facts are explained by the hypothesis that the inter-cellular substance consists of a complicated quinone which is intimately associated with a carbohydrate . . . more closely allied to cellulose than to glucose."

This view we are now in a position to confirm and develop from results which we have recently obtained by graduated oxidations of the ligno-celluloses with chromic acid. Of these we take the opportunity of giving a brief preliminary notice.

Chromic acid, in cold dilute aqueous solution, is not de-oxidised to Cr_2O_3 by the jute fibre substance; there appears, on the other hand, to be a direct combination and a considerable quantity of the oxide appears to be fixed,

* We also obtain methyl chloride by the destructive distillation of the chlorinated derivative of the lignone of jute.

probably, in part at least, in the form of the oxides intermediate between CrO_3 and Cr_2O_3 .

The addition of a mineral acid determines the de-oxidation, and the fibre is converted into a greenish product, brittle and yet soft to the touch, and of high lustre. Of this product we obtain from 85–90 per cent of the weight of the raw fibre; in this case a jute of medium quality, yielding about 74 per cent cellulose by the ordinary chlorination method. On ignition it gives an ash containing Cr_2O_3 , equal to from 2–2.5 per cent of its weight. The organic portion we find to be an *oxycellulose*. The carbon percentage we have determined in various specimens; it varies between 43 and 44. It is largely soluble in alkalis, the solution reducing Fehling solution copiously on boiling.

Pine-wood we find gives similar results, i.e., a high percentage of a product of low carbon percentage, soluble for the most part in cold alkaline solutions, and agreeing in this as in other respects with the well-characterised group of *oxycelluloses*.

The soluble products of the chromic acid oxidation we have isolated and find to be brown gummy bodies, giving chlorine substitution products with characteristic colour reactions.

By this particular oxidation, therefore, we appear to convert into cellulose (i.e., a derivative of cellulose) a body which, under the treatment hitherto adopted for separating the cellulose, is *hydrolysed* into soluble products. We have on many occasions pointed out that the yellow chlorinated derivative obtained from the fibre contains a *quinone-chloride* associated with a body which gives a copious yield of fufural by acid hydrolysis, and probably, therefore, a *pentaglucose*.

It is therefore probable that this pentaglucose exists in the fibre in the form of a cellulose (Comp. E. Schulze, *Berl. Ber.*, xxiv., 2277).

There are many grounds for regarding lignification as a process of modification of cellulose by deoxidation and dehydration, and the action of dilute chromic acid in presence of a hydrolysing acid would appear to confirm this view, while giving the nearest approach which we have yet made to the retracing of the process backwards through its several stages.

We are engaged in following up these observations, which cannot fail to afford many new links in the chain of evidence by which the celluloses are being connected with bodies of definite constitution.

Laboratory, 4, New Court, London, W.C.
July 30, 1891.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 53).

XIV.—Cadmium.

1. With sodium bicarbonate. Round granules of 2–3 micro., diameter refracting light strongly (see Zinc i). On account of the finely granular texture of the precipitate, the deposition of cadmium by sodium bicarbonate is decisive, only if performed in an ammoniacal solution from which magnesium, nickel, &c., have been previously removed by means of phosphorus salt. Limit of the reaction at 0.0001 m.grm. Cd.

2. With oxalic acid. Rhombs and parallelopipeds of the oxalate $\text{Cd}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$, belonging to the monoclinar system, twice as large as the crystals of zinc oxalate, extinguishing at 24° . If more than 30 per cent of zinc are present the form of zinc oxalate prevails exclusively. Limit of the reaction at 0.0034 m.grm. Cd.

The solution of cadmium oxalate in ammonia yields

on evaporation rods and tables, but in presence of zinc sphærolites which present nothing characteristic. Acids and salts of aluminium, chrome, and iron prevent the precipitation of cadmium oxalate. The cadmium may be conveniently thrown down from an ammoniacal solution as under 1, and after drawing off the ammoniacal liquid the granular precipitate can be converted into the crystalline oxalate by adding a granule of oxalic acid.

3. With ammonium-mercury sulphocyanide. Massive, rectangular prisms and pseudopyramids, in presence of zinc, merely the forms of zinc-mercury sulphocyanide. With cobalt blue mixed crystals. Limit of the reaction at 0.001 m.grm. Cd.

4. With potassium ferricyanide. Yellow, cubic crystals of 3–4 micro., not distinguished from those of zinc ferricyanide. Limit of the reaction at 0.00003 m.grm. Cd.

Metallic magnesium precipitates zinc and cadmium readily and completely from slightly acidulated solutions. From the grey metallic sponge the chief part of the zinc may be extracted by boiling acetic acid.

XV.—Cerium, Lanthanum, Didymium.

1. With sodium sulphate. Heavy, white precipitate of a crystalline structure, the formation of which in dilute solutions is promoted by heat. Strong acids, especially sulphuric acid, interfere. The precipitate consists of small lenticular discs and rounded rods, varying in length from 4 (for Ce) to 10 micro. (Di). Potassium sulphate throws down discs of 4–6 micro. Thallous sulphate slowly precipitates hexangular colourless tables up to 100 micro. All these double salts are decomposed by sodium carbonate, potassium ferrocyanide, and oxalic acid. Limit of the precipitation—

For Ce at 0.00002 m.grm.

„ La „ 0.00004 „

„ Di „ 0.00007 „

2. With sodium carbonate. Flocculent precipitates, that of lanthanum whitish, the others in transmitted light brownish. In an excess of the reagent crystallisation ensues in time. Lanthanum carbonate is, after half an hour, completely converted into pale, oval leaflets and thistle heads of 40–70 micro. Cerous carbonate forms more slowly spiked globes and acute rhombs of 10–40 micro. Didymium carbonate requires at least an hour, and the crystallisation does not extend beyond the formation of crystalline nodules of 12–20 micro. Limit of the reaction for Ce at 0.00005 m.grm., for La 0.00006 m.grm., for Di 0.0001 m.grm.

3. With oxalic acid we obtain at first white, pulverulent precipitates, which in an excess of the precipitant quickly become fine needles. Cerium yields after a few minutes crosses of 70, and imperfect squares of 40 micro. Lanthanum yields needles and prolonged rhombs of 60 micro. grouped in sheaves. Didymium produces crosses and sphærolites like cerium. Limit of the reaction for cerium 0.00004 m.grm.; for lanthanum 0.00006 m.grm., for didymium at 0.0001 m.grm.

4. Potassium ferrocyanide produces granular precipitates. With cerium transparent, colourless grains of 4–6 micro., and partly rounded cubes. With lanthanum clear rhombs of 50 micro. An excess of the reagent modifies them into barrel-shaped prisms, and deposits colourless hexagons and hexagonal prisms of 30–60 micro. With didymium hexagons with depressed angles, rosettes radially ribbed, stars and dendrites of about 60 micro. The largest specimens are distinctly violet-grey. Limit of the reaction for cerium and lanthanum at 0.0001 m.grm., for didymium 0.00015 m.grm.

For distinguishing the cerium metals, methods of separation must be used. From the mixed oxalates, or by melting the double sulphates with soda, mixed oxides may be obtained from which dilute nitric acid chiefly extracts lanthanum and didymium, the solution may then be evaporated, and the bulk of the didymium nitrate may be decomposed by cautious fusion. For further exami-

* *Zeit. Anal. Chemis.*

nation the reactions 2 and 4 are to be preferred. 0.1 grm. of the mixed double sulphate is a sufficient quantity for separation.

XVI.—Yttrium-Erbium.

1. Oxalic acid precipitates neutral and faintly acid solutions in the state of extremely fine crystals. By means of a plentiful addition of hydrochloric acid crosses of 25 micro. may be obtained. The limit of the reaction is at 0.005 m.grm. Y.

2. If the oxalate is dissolved in ammonium carbonate, tetragonal pseudo-octahedra are obtained of 10–25 micro. If to a solution of yttrium-erbium carbonate in ammonium carbonate there is added a little ammonium oxalate, the finely crystalline precipitate may be converted into the ordinary crystals by repeated heating, and replacing the water and ammonium carbonate which have been expelled. The reaction in this form is very useful.

(To be continued.)

CONTRIBUTIONS TO THE CHEMISTRY OF ERBIUM AND DIDYMIUM.*

(FIRST COMMUNICATION.)

By GERHARD KRÜSS.

AMONGST the least readily accessible departments of inorganic chemistry must doubtless rank the chemistry of the metals of the rare earths. Most distinguished inquirers—Berzelius, Mosander, Bunsen, Marignac, Rammelsberg, Cleve, Nilson, Petterson, Brauner, and others—have carried on extensive researches on the metals of the cerium and yttrium group, and yet our knowledge of many of the rare earths is still but fragmentary. Thus, for instance, the oxides of terbium, thulium, and holmium are hitherto approximately diagnosed by few characters only, and it is even questionable if these earths are unitary bodies. Even erbium and didymium, whose oxides rank with the earths which have been most closely studied (at least among those which produce absorption spectra), are as yet by no means certainly characterised, and cannot be introduced with certainty into the natural system of the elements.

If, despite the most strenuous labours of many inquirers, the veil which still enshrouds the true nature of erbium and didymium has been raised only partially and slowly, time spent in this region of chemistry did not seem to promise, *a priori*, any rapid and abundant scientific returns. Still the author has ventured to penetrate a little further into the chemistry especially of erbium and didymium, the rather as the periodic system is but imperfectly developed in its middle series, to which erbium and didymium—or perhaps their constituents—must belong. These researches were supported most liberally by The Elizabeth Thomson Science Fund, for which the author here returns his best thanks to the Trustees of that Foundation.

In the following treatise are given the results of certain experiments made for the purpose of discovering more convenient methods for isolating the earths, as well as certain means for diagnosing the erbium and didymium hitherto so called.

At present we understand by the names erbium and didymium different bodies from those which were so called in the years 1870 to 1880. That oxide which about twenty years ago was known as erbia, and was regarded as the oxide of an individual earth, consists—according to the interesting researches of Marignac, Soret, Nilson, Cleve, Brauner—of at least seven distinct earths, scandia, ytterbia, thulia, erbia, terbia, Soret's X, and yttria. Further, a few years ago, Lecoq de Boisbaudran, by the

fractionated precipitation of Soret's X and the spectroscopic examination of the several fractions, showed that X, or Cleve's holmium, consists of at least two elements. It further results, from the interesting researches of Crookes, that yttria is not the oxide of a chemical individual.

Thus "old" erbium has gradually been resolved into an extensive series of elements. A similar lot has occurred to that body which, in the last decennium, was known simply as didymium. This also has been broken up, firstly into D β (Brauner's Z), or samarium and true didymium; and the latter, again, as it appears from the researches of Auer von Welsbach, consists of at least two distinct elements, neodmium and praseodymium.

Such was the condition of the chemistry of the rare earths when, some time ago, L. F. Nilson and the present writer demonstrated—by a spectroscopic examination of the rare earths obtained from the thorites, euxenites, fergusonites, wöehlerites, and cerites of different localities—that the rare earths which yield absorption spectra (erbium, holmium, thulium, didymium, samarium) consist of a far greater number of components than it might be assumed from the investigations of Soret, Lecoq de Boisbaudran, Auer von Welsbach, and others. The spectroscopic examination of the several fractions obtained by the fractionated decomposition of the nitrates of the earths of fergusonite and euxenite proved how impossible it is *completely* to resolve the entire erbia and didymia into its separate constituents by the often-employed method of a partial decomposition of the nitrates. This is especially the case if we have at our disposal only a few kilos. of initial material. (For the detailed results of this investigation the reader is referred to *Ber. Deutsch. Chem. Gesell.*, xx., 2134.)

As little did Lecoq de Boisbaudran succeed in a complete resolution of Soret's X by a combination of the fractionated decomposition (by heat) of the nitrates, and fractionated precipitation of the solutions of the nitrates with ammonia. Even Auer von Welsbach's method of a fractionated crystallisation of the double ammonium nitrates in a strongly acid nitric solution was not capable of entirely resolving didymium into its individual constituents. According to the experiments of Krüss and Nilson, neodmium and praseodymium are still compound bodies. This observation was confirmed by the researches of A. Bettendorff on the earths of the cerium and yttrium groups recently published in the *Annalen* (cclvi., p. 159).

Hence up to the present date we have not yet succeeded in completely isolating any one constituent of the rare earths which yield absorption spectra, and characterising it with certainty as an element. The very slightly differing basicity of these earths, and the solubilities of their salts, which are almost alike, impede in the highest degree the solution of this problem.

Elsewhere (*Ber. Deutsch. Chem. Gesell.*, xxi., p. 2310) the author has pointed out that we may approach nearer to our purpose if we observe that nature has deposited some or other constituents of the rare earths which yield absorption spectra, together or separate in one or other mineral, as obtained from this or that locality.

It appeared, also, from the researches on the components of the rare earths by Krüss and Nilson, quoted above, that *e.g.* of the simple constituents of the "old" earth X, which have been named X α , X β , . . . X η , the nitrate solutions of which display in their spectrum characteristic absorption bands, there occur in—

Mineral.	Only the Elements.
Thorite from Brevig . . .	X α , X δ , X η .
Arendal . . .	X β , X γ , X ϵ , X ζ , X η .
Wöehlerite from Brevig . . .	X γ , X ζ , X η .
Cerite from Bastnäs . . .	X α , X η .
Fergusonite from Arendal . . .	X β , X γ , X δ , X ϵ , X ζ , X η .
Ytterby . . .	X α , X β , X γ , X δ .
Euxenite from Hitterö and Arendal	X ϵ , X ζ , X η .

* Liebig's *Annalen*.

Nature has thus effected a partial separation of these elements which approximate so closely in their properties, and, in order as far as possible to utilise this fact in the further study of the rare earths, it seemed advantageous to institute a further spectroscopic revision of the basic constituents of rare minerals from the most different localities. For this purpose there were utilised the above-mentioned researches of Krüss and Nilson, and from this point of view experiments have been recently made by P. Kieseewetter and G. Krüss.

In addition to a series of thorites, euxenites, fergusonites, wöhlerites, cerites, keilhauites, and monazites, from different localities, the author has made the closest spectroscopic examination of a number of other minerals in search of the earths of the erbium and didymium earths, and he has undertaken by the best-known methods to isolate one or the other constituent of erbium or didymium from the minerals where it seemed most richly accumulated. It is certainly possible in this manner to obtain peculiar spectra of erbium and didymium, and abnormal spectra of holmium, in which the relative intensities of the several absorption lines are quite different from those commonly occurring. But I must admit that, whilst using the accepted methods of separation for the rare earths, I have never succeeded in obtaining perfectly unitary, homogeneous bodies, the molecular weights of which remained absolutely constant on further treatment.

When, *e.g.*, I had succeeded in obtaining a few grms. of a didymium earth which displayed in the absorption spectrum of its nitric solution almost *one* only double band in the green, and if then large quantities of the same didymia earth were prepared in the same manner, there appeared, on the spectroscopic examination of a more concentrated solution in a stratum of several decimetres in thickness, along with the extremely intense double band in the green, a series of other very faint lines of absorption.

Without doubt we are still in want of methods for the separation of the rare earths which are even approximately exact, and some of the methods hitherto applied have not been developed in a trustworthy manner. Considerable weights, therefore, of crude material were used, and in obtaining ordinary erbia and didymia a series of methods of separation, partly new and partly old, were studied. The oxides, as obtained by different methods, were always carefully examined for their homogeneity, both spectroscopically and by a determination of their molecular weights.

Preparation of Erbium and Didymium Salts from Gadolinites, avoiding the method of fractionating the rare earths by long series of decompositions, by heating their nitrates:—

In order to separate erbium from didymium, the method proposed by Mosander and developed by Bunsen has generally been applied, depending on the different solubility of the double potassium salts of both earths. This method by no means admits of an exact separation of the didymium from the yttrium earths. Even if the solution of the mixed earths is saturated for several days with potassium sulphate, until there no longer appears any precipitate of the double sulphates, several didymium lines may still be observed in the spectrum of the yttria earths, and erbium and holmium lines on the spectrum of the earths precipitable by potassium sulphate. (See Krüss and Nilson, *Ber. Deutsch. Chem. Gesell.*, xx., p. 2140). Nilson previously (*ibid.*, xv., p. 2525) pointed out the imperfection of this method of separating didymium from the yttria earths.

That there exists a very considerable difference in the respective solubilities of the double sulphates of potassium, didymium, and erbium is indubitable; it had therefore to be tried to separate erbium from didymium by fractionated crystallisation with potassium sulphate. The results which Dr. K. Bröckelmann obtained in some experiments of this kind were as follows:—

Hot concentrated acid solution of potassium sulphate was added to the faintly acid solution of the nitrates of the rare earths until a crystalline precipitate appeared. It was filtered off hot, and washed with hot concentrated solution of acid potassium sulphate until the washings no longer produced a precipitate with ammonia. The washings were mixed with the filtrate, the solution again precipitated in the same manner, and this treatment was repeated until an excess of potassium sulphate added to the filtrate of the last precipitate no longer determined a precipitate.

(To be continued.)

THE DETERMINATION OF CARBON IN STEEL.*

By A. A. BLAIR.

PROF. J. W. LANGLEY has given in his excellent paper (*Journal of Analytical and Applied Chemistry*, vol. iv., p. 403), read at the joint session of the American Institute of Mining Engineers, and the British Iron and Steel Institute at Pittsburgh, a clear history of the first part of the work of the American members of the International Steel Standards Committee in their investigation of the various methods for the determination of carbon in steel.

As regards the combustion method, the results as stated by Prof. Langley may be briefly summarised as follows:—Dr. Dudley showed in a most interesting series of results that the double chloride of copper and ammonium contained some form of organic matter which united with the carbonaceous matter liberated from a steel by the action of this solvent, the amount of the organic matter varying with the purity of the double chloride, and diminishing with each crystallisation of the salt. The remarkable fact which I discovered, that a very acid solution of the double chloride gave higher results than a neutral solution, was quickly verified by both Prof. Langley and Dr. Dudley. Dr. Dudley thought that the acid caused a precipitation of organic matter from the double chloride, while my view was that a neutral solution is rendered slightly alkaline by the solution of the metallic iron and the precipitated copper, and that this alkaline solution dissolves some of the carbonaceous residue which is not subsequently precipitated by the addition of acid.

It was agreed, after the reading of Prof. Langley's paper, that I should continue this investigation, and the results have proved of so much interest to the American Committee that it is deemed advisable to make them public now, that the profession at large may have the benefit of the suggestions they offer without undue delay.

My combustion apparatus consists of a platinum tube 26 inches long and 9-16 of an inch in diameter, the forward part inside the furnace being filled for a distance of six inches with granulated oxide of copper held in place by two plugs of platinum gauze. A plug of platinum gauze completely filling the bore of the tube is inserted after the boat, and occupies the portion of the tube at the rear of the furnace.

The oxygen and air are contained in cylinders under pressure, and each passes through its own purifying apparatus consisting of a bulb containing caustic potassa, 1·27 specific gravity, followed by a 12-inch U-tube containing broken pieces of pumice stone. Following each U-tube is a tube fitted with a glass stop-cock leading into a T-tube which connects directly with the end of the combustion tube. By this arrangement the oxygen and air are under perfect control, and there is no danger, as in the ordinary manner of drawing the air through the apparatus by means of an aspirator, of introducing into it any gases that may be in the laboratory. The purifying train for the products of combustion consists of a U-tube contain-

* From the *Journal of Analytical and Applied Chemistry*, Vol. v., No. 3, March, 1891.

ing in the limb nearest the combustion tube anhydrous sulphate of copper in pumice, and in the other, turnings of metallic copper, followed by another U-tube containing chloride of calcium. In the absorption apparatus the ends of the Liebig bulb and one end of the tube are fitted when on the balance with short pieces of very fine capillary glass tubing; the other end of the tube is fitted with a cap of rubber tubing, the outer end of which is squeezed together and cemented. This arrangement allows the passage of sufficient air to equalise the pressure in the absorption apparatus, but the capillary openings are too small to permit the loss or gain of moisture during the operation of weighing.

In all cases I used the "factor" weight of the drillings (2.7273 grms.), so that each 0.0001 gm. of carbonic acid obtained in the absorption apparatus is equal to 0.001 per cent of carbon in the steel.

I determined in the first place to repeat Dr. Dudley's experiments on the re-crystallisation of the double chloride of copper and ammonium, and therefore prepared a solution by mixing commercial chloride of copper and chloride of ammonium, adding ammonia until a slight precipitate formed, allowing this to settle, syphoning off the clear solution and filtering it through ignited asbestos. This I called solution "A."

Using 200 c.c. of solution "A" and 20 c.c. hydrochloric acid, I obtained:—

No. 1, carbon		1.046 per cent.
" 2, "		1.047 "
" 3, "		1.044 "
" 4, "		1.049 "

Using 200 c.c. solution "A" without the addition of hydrochloric acid, keeping the solution as neutral as possible, and washing with acidulated solution "A" to get rid of the basic salts, I obtained:—

No. 5, carbon		1.013 per cent.
" 6, "		1.004 "

I then evaporated solution "A," and crystallised the double chloride. I washed each crop of crystals with cold water, and finally reserved the mother-liquor, which I filtered through ignited asbestos, calling it solution "B." The crystals dissolved in water and filtered through asbestos I called solution "C." Using 200 c.c. of solution and 20 c.c. hydrochloric acid I obtained:—

Solution "B."

No. 7, carbon		1.076 per cent.
" 8, "		1.067 "

Solution "C."

No. 9, carbon		1.027 per cent.
" 10, "		1.029 "

I then crystallised about a gallon of the solution which I have in constant use, which is made by dissolving the salt that I buy as "c. p. crystallised double chloride of copper and ammonium," in water, adding slight excess of ammonia, allowing to stand for several days, syphoning off, and filtering the clear liquid through ignited asbestos. The mother-liquor that I obtained I called solution "D," and the solution of the re-crystallised salt solution "E," with which I made two determinations, adding 15 c.c. hydrochloric acid to one, and leaving the other neutral with the following results:—

Solution "D."

No. 11, (acid) carbon		1.064 per cent.
" 12, neutral carbon		1.022 "

Solution "E."

No. 13, (acid) carbon		1.028 per cent.
" 14, (neutral) carbon		0.998 "

I then prepared a solution of chloride of copper by igniting 250 grms. of pure oxide of copper in platinum at a red heat for thirty minutes, dissolving in hydrochloric acid, evaporating to dryness, re-dissolving in water, and filtering through asbestos. The solution which contained 28 grms. of cupric chloride to 100 c.c. I called solution "F." With this I made four determinations, two with 20 c.c. of hydrochloric acid added to the solution, and two with the solution kept as neutral as possible.

Solution "F."

No. 15, (acid) carbon		1.034 per cent.
" 16, " "		1.034 "
" 17, (neutral) carbon		1.034 "
" 18, " "		1.033 "

It required two days to effect solution in the acid determination, and three days in the alkaline, with constant stirring.

I then made four determinations, using 125 c.c. of solution "F," 15 c.c. hydrochloric acid, and 1, 2, 3, and 4 times the molecular equivalent of chloride of ammonium. The latter I made by neutralising C. P. hydrochloric acid with C. P. ammonia. The results are as follows:—

P. c.

No. 19, (1 equiv. of chloride of ammonium) carbon	1.038
" 20, (2 " " " " " "	1.055
" 21, (3 " " " " " "	1.055
" 22, (4 " " " " " "	1.073

I then fused chloride of potassium, and added it to 125 c.c. portions of solution "F" with 15 c.c. hydrochloric acid, with the following results:—

P. c.

No. 23, (1 equiv. of chloride of potassium) carbon	1.036
" 24, (2 " " " " " "	1.036

Solution of the drillings with the potassium salt is as rapid as with the ammonium salt, occupying about twenty minutes with the "special carbon standard."

I now determined to try the direct combustion of the steel in oxygen, and for this purpose I had a platinum boat made six inches long, and just large enough to go in my combustion tube. I had a cover of platinum foil made for the boat with a half circle cut through about every half inch. On raising these semi-circular pieces to an angle of about 45°, they made a series of little wings which directed the current of gas flowing along the top of the tube down into the boat. I selected for this purpose the finer portion of the drillings, and after the combustion I withdrew the boat, ground the magnetic oxide in an agate mortar to expose any metallic particles that might remain unacted upon, and burned it a second time. In no case did I get the slightest increase in the weight of my absorption apparatus by the second combustion.

No. 25, carbon		1.031 per cent.
" 26, " "		1.020 "
" 27, " "		1.024 "
" 28, " "		1.032 "

Finally I made a determination of carbon by volatilising the iron in a current of dried hydrochloric acid gas which had been passed through a porcelain tube filled with charcoal and heated to bright redness. This gave me:—

No. 29, carbon		1.024 per cent.
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I then procured from a firm of manufacturing chemists a lot of crystallised double chloride of copper and potassium, and made a solution by dissolving 300 grms. of the salt in a litre of water and filtering through ignited asbestos. Using 200 c.c. of this solution and 15 c.c. strong hydrochloric acid, I obtained:—

No. 30, carbon		1.035 per cent.
" 31, " "		1.038 "

Dr. Dudley's theory of the double chloride of copper

and ammonium containing organic matter, which is liberated in the treatment of steel, attaching itself to the carbonaceous residue, and thus increasing the apparent carbon contents of the steel, seems proved by his own determination as well as by the results Nos. 7, 8, 11, 19, 20, 21, and 22; the last four results led me to believe, however, that this organic matter comes from the chloride of ammonium, and is a hydrocarbon derived from the gas liquor from which all ammonia salts are now made.

My own theory, that the copper solution must be strongly acidified to give correct results, received strong support from the determinations Nos. 5, 6, 12, and 14; for these, as well as my previous determinations, point strongly to a solution of the carbonaceous matter by the alkaline salts in the absence of an excess of acid. The striking results obtained from the chloride of copper solution "F" show plainly that an excess of acid does not cause a loss of carbon, while it very much facilitates the solution of the steel. I then obtained from Prof. Langley some very fine drillings of the same steel, and using the six-inch boat described above I obtained:—

No. 32, carbon	1.032 per cent.
" 33, "	1.030 "
" 34, "	1.031 "

To test the effect of using a purifying apparatus that had been used for combustions of the carbonaceous residue liberated by the double chloride, I made several combustions of these residues and, without changing the apparatus, a direct combustion. The result was:—

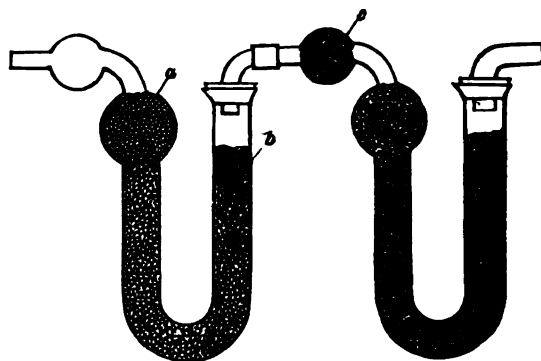
No. 35, carbon	1.042 per cent.
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This last result, taken in connection with many others that I had previously obtained, suggested to me the desirability of using some substance in my purifying apparatus that would not only prove more efficient, but would render unnecessary the constant changes and delays involved by a number of sets of purifying tubes and the necessity for changing the anhydrous cupric sulphate in pumice. It has been my practice to use one set of purifying tubes for three combustions only, then to substitute another set, and while this was in use to purify the first set by placing the limb of the U-tube that contained the cupric sulphate in a copper box, heat the box to about 200° C., and draw air, previously dried by passing it through a jar of chloride of calcium, through the apparatus. I therefore instituted a series of experiments on this subject, being finally led to try cuprous chloride on the theory that small amounts of hydrochloric acid gas and chlorine, when brought in contact with cuprous chloride, would be absorbed, the chlorine oxidising the cuprous to cupric chloride. I then prepared a purifying train consisting of two Marchand U-tubes, the first of which contains in the bulb *a* granulated dried cuprous chloride, made by moistening the ordinary powdered salt and stirring it while drying in a capsule, until it forms into little lumps about the size of a split pea. After heating it until all the moisture is expelled it is transferred, while still hot, to the U-tube, completely filling the bulb *a*. The rest of the U-tube is filled with anhydrous cupric sulphate made by heating small crystals of the ordinary salt until the water is expelled and the salt is white. At *b* is placed a plug of asbestos to prevent small particles of cupric sulphate from being carried forward with the current of gas. The second U-tube is filled with *dried*, not fused, chloride of calcium, as the latter is apt to contain caustic lime. Cupric sulphate absorbs its own volume of hydrochloric acid gas, giving it up only when heated. With the tubes thus filled I made four combustions on the "special carbon standard ingot," using the double chloride of copper and potassium, and washing No. 36, 37, and 38 with hot hydrochloric acid and water, and No. 39 in the usual way, using cold water and acidulated double chloride. Mr. Shimer thought that by washing with hydrochloric acid and hot water there

was less hydrochloric acid left in the carbonaceous residue, and I wanted to see whether there was any possibility of getting lower results in this way due to the action of the acid and hot water on the carbonaceous residue.

No. 36, carbon	1.030 per cent.
" 37, "	1.029 "
" 38, "	1.033 "
" 39, "	1.026 "

The results were all low, and I should have been inclined to refer it to the method of washing, but that No. 39, washed in the usual way, was the lowest of all. It then occurred to me that anhydrous cupric sulphate being much more hygroscopic than chloride of calcium, the oxygen and air left the absorption apparatus with more moisture than they had when they entered it after passing through the purifying train. If this were true then the



greater the volume of oxygen and air passed through the apparatus, the lower the result. To prove this I made a direct combustion on the fine sample, the time occupied being about ninety minutes instead of the usual thirty-five minutes necessary to burn the carbonaceous residue. The combustion followed immediately after No. 39, the result being:—

No. 40, carbon	1.006 per cent.
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This seemed quite conclusive as to the cause of the low results, and to overcome the difficulty I introduced a small plug of cotton into the bulb *c* of the chloride of calcium tube, and moistened it with one or at most two drops of water. Another direct combustion on the fine sample gave:—

No. 41, carbon	1.037 per cent.
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I then made a number of combustions in the course of my ordinary work, removing the plug of cotton in *c* after each day's work, and putting in a fresh one duly moistened before each new set of combustions. After the lapse of several days I made two more determinations on the "special carbon standard ingot," No. 42 on the carbonaceous residue and No. 43 a direct combustion. They were respectively the fourth and fifth combustions of a series made at one time, and No. 43 was the twenty-third combustion made without heating the purifying apparatus.

No. 42, carbon	1.038 per cent.
" 43, "	1.037 "

I am led to conclude that chloride of copper and potassium is a much more safe and desirable solvent to use than chloride of copper and ammonium, and unless subsequent experience shall show some flaw in my work, cuprous chloride and anhydrous cupric sulphate are much more convenient and much safer reagents for purifying the gas than any substances previously used.

This series of experiments illustrates in a striking way the value of a "standard" in work of this character. The carbon once established in a sample, each experiment has an increased value, for the result is known to be not only a departure from the mean of many analyses, but a variation from the absolute amount. The value of a method or the deficiency of an arrangement of apparatus is thus made evident at once, and the error is much more readily referred to its real source than would otherwise be possible.

Analytical chemists all over the world will owe Prof. Langley a debt of gratitude, not only for his suggestion that led to the establishment of the International Committee, but for his subsequent work which has made it possible to carry out his original idea.

THE BIOLOGICAL FUNCTION OF THE LECITHINES.

(PRELIMINARY NOTICE).

By W. MAXWELL.

IN an earlier stage of the study of the lecithines I showed, in an article entitled "On the Behaviour of the Fatty Bodies, and the Role of the Lecithines During Normal Germination" (*American Chemical Journal*, xiii., No. 1), that the inorganic phosphorus present in the mature seed, under the action of the processes occurring during incipient growth, becomes re-organised, and appears in the young plantlet in the organic form as a constituent of lecithine.

In the course of continuation of the researches, which have been extended or carried over from the vegetable to the animal organism, I have established the observation that the phosphorus which is present in the organic form as a lecithine in the egg of a hen, under the action of the process of incubation, becomes re-organised, and is found in the form of a mineral phosphate in the bone of the chicken.

In the light of the data to be given in a later contribution, of which this is a preliminary notice, it will be possible to indicate the course of the circulation of the element phosphorus in the three divisions of matter, and to show that it is (at least in great part) in the organic form of the lecithine, or lecithines, that the inorganic phosphorus of the mineral kingdom passes through the vegetable kingdom into the inorganic form, constituting the bone, of the animal kingdom.—*American Chemical Journal*, xiii., No. 6.

ON THE ACTION OF 66° SULPHURIC ACID ON HYDROCHINON, AND THE VALUE OF THE RESULTING SULPHO-ACID AS A DEVELOPER FOR GELATINO-BROMIDE PLATES.

(PRELIMINARY NOTICE.)

By JAMES H. STEBBINS, JUN.

SINCE the introduction of the dry plate in photography many substances have been proposed as developers, but the only practical survivors of the substances thus proposed are pyrogallol acid, ferrous oxalate, hydrochinon, and more recently eikonogen, or the sodium salt of amido- β -naphtholmonosulpho acid. Having at one time had occasion to employ hydrochinon as a developer, I was struck with the beautiful qualities of the plates developed by its means, but, although hydrochinon is *per se* a most excellent developer, it has, nevertheless, several drawbacks, among which are its limited solubility in water, and it was this very question of solubility which started

me upon the present investigation. It seemed that if hydrochinon could be converted into a mono-sulpho acid, that its solubility would be very materially increased, and if this could be accomplished without in any way affecting its reducing qualities for the haloid salts of silver a very material improvement would be obtained.

Finding only very meagre information in the literature upon this subject, the following experiments were made:—

Experiment 1.

Twenty grms. of 66° sulphuric acid were mixed with 10 grms. of hydrochinon, and then heated under constant stirring upon the steam bath, until the hydrochinon was all dissolved. The stirring was kept up for a few minutes longer, when suddenly the whole contents of the beaker solidified to a cake of small straw-coloured needles.

The cake was broken up and dissolved in cold water, in which it is very soluble; then converted into its lime salt by neutralising the acid solution with calcium carbonate. The precipitate of calcium sulphate was filtered off, and the filtrate of the lime salt placed upon the steam bath for concentration. After a short exposure to the air the solution began to darken, showing that oxidation was taking place. Concentration by this means had therefore to be abandoned. The solution was then placed under the air-pump over sulphuric acid, hoping that by this means it may be concentrated without spoiling, but even in this case oxidation kept slowly taking place. It was therefore decided to treat the mixture with an excess of sodium sulphite, and then concentrate *in vacuo* over sulphuric acid. On adding the sodium sulphite, calcium sulphate was precipitated, carrying considerable of the colouring-matter with it. The precipitate was filtered off, and the filtrate containing the sulpho-acid of hydrochinon was placed under the bell jar of the air-pump over sulphuric acid, to concentrate, but owing to an accident the contents of the beaker were spilled, and therefore the experiment had to be repeated.

Experiment 2.

Ten grms. of hydrochinon were treated as before, with 20 grms. 66° sulphuric acid. After the reaction the mixture was dissolved in water, heated upon the water-bath, and neutralised with barium carbonate.

The barium sulphate was filtered off, and the filtrate containing the barium salt of the sulpho-acid was concentrated *in vacuo* over sulphuric acid. The barium salt thus obtained crystallised much more readily than the calcium salt, and the solution of the same in water does not appear to be as readily oxidisable as the former when exposed to the air. It crystallises from its aqueous solution in white, warty, concretions of star-grouped crystals (needles).

A sample of the above barium salt, obtained by rapidly boiling down a portion of its aqueous solution to dryness and then further drying over sulphuric acid, gave the following results:—

Water of Crystallisation.

0.2810 grm. substance lost 0.0081 grm. H_2O .

Equivalent to water 2.88 per cent., or 1 mol. water of crystallisation.

Ba Estimation.

0.2810 grm. sub. gave 0.116 grm. $BaSO_4$.

Equivalent to Ba 24.26 p. c.

Equivalent to Ba in anhydrous salt . . . 24.98 „

On now attempting to calculate the molecular weight of the barium salt from the amount of barium sulphate formed, we get the following:—

0.2729 anhydrous salt gave 0.116 grm. $BaSO_4$.

0.116 : 233 ($BaSO_4$) :: 0.2729 : x ; x = 548.1.

The least molecular weight of the salt, carrying one atom of barium, is therefore 548.1.

One atom of barium might belong, however, to a substance containing either one or two sulpho-groups: but the theoretical molecular weight of barium hydrochinon disulphonate is 406, whereas the theory for barium hydrochinon monosulphonate is 515 (calculated from the

formulae ($p. C_6H_3 \begin{smallmatrix} \text{OH} \\ \text{---} \text{SO}_3 \end{smallmatrix} \text{Ba}$), and consequently

the former is excluded. Therefore the substance analysed is beyond much doubt the barium salt of a hydrochinon mono-sulpho-acid.

On calculating the molecular weight from the salt containing water of crystallisation we get—

$$0.116 : 233 :: 0.281 : x; x = 564.$$

The theoretical molecular weight of the hydrated salt, or rather salt containing water of crystallisation, is 533.

The theoretical amount of barium called for in the anhydrous salt is 26.6 per cent.

The theoretical amount of barium in the hydrated salt is 25.7 per cent.

The amount of water of crystallisation found is 2.88 per cent; therefore—

$$2.88 : 18 :: 0.16 \text{ mol. } H_2O.$$

That is to say, that 100 parts of barium salt contain 0.16 mol. H_2O of crystallisation; therefore 548 parts of barium salt will contain—

$$100 : 0.16 = 548 : 4; 4 = 0.87 \text{ mol. } H_2O,$$

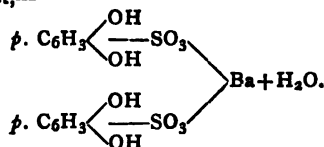
or, in round numbers, 1 mol. H_2O . We have therefore found—

Barium	24.26 per cent.
Water of crystallisation ..	2.88 "
Molecular weight	564.

Whereas theory calls for—

Barium	25.7 per cent.
Water	3.40 "
Molecular weight	533.

The formula of the barium salt is therefore, without much doubt,—

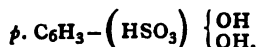


The barium salt is readily soluble in cold water and dilute alcohol, and insoluble in strong alcohol. It crystallises from dilute alcohol in white six-sided prisms. On adding ferric chloride to its aqueous solution, a momentary deep blue colouration is obtained, which, almost immediately, changes into a dirty yellow colour.

Potassium Salt.

This salt was obtained from the barium salt, by decomposing the latter with the theoretical amount of potassium carbonate. On rapidly concentrating the aqueous solution of the same, out of contact with the air as much as possible, it is obtained in the shape of little yellowish-white needles. Better results, however, are obtained by adding three or four volumes of alcohol to the concentrated aqueous solution, and then allowing the mixture to evaporate under the bell jar of an air-pump. It is readily soluble in water.

Free Acid.



The free acid may be obtained from the barium salt by accurately decomposing the latter with dilute sulphuric acid, filtering off the $BaSO_4$, shaking up the filtrate with ether, and then distilling off the latter and allowing to crystallise. A simpler method, and one that works very well, is to place the cake resulting from the action of

H_2SO_4 upon the hydrochinon, upon porous tiles, till the greater part of the excess of sulphuric acid has been absorbed. Then press the mass between filter-paper until nearly every trace of H_2SO_4 has been removed. The mass thus obtained is dissolved in as little alcohol as possible, and set aside to crystallise under the air-pump. The free acid is thus obtained in long, well-defined, brownish, transparent, rhombic prisms (some of the crystals were over 1 c.m. long), containing alcohol of crystallisation. When exposed over sulphuric acid it effloresces, giving off a part, or all, of its alcohol of crystallisation.

0.1155 grm. substance over H_2SO_4 lost 0.0087 grm. alcohol, = 753 per cent. On now heating to $120^\circ C$. the said free acid lost 0.004 grm. more of alcohol. It will therefore be seen that the larger part of the alcohol of crystallisation is lost over H_2SO_4 .

The total amount of alcohol lost is therefore $0.0087 + 0.004 = 0.0127 \text{ grm.} = 10.9 \text{ per cent.}$

This equals 0.43 molecule, or, in round numbers, one-half molecule alcohol of crystallisation.

Theory for $C_6H_3(HSO_3)(OH)_2$. One-half C_2H_6O calls for alcohol 10.7 per cent.

It begins to fuse at $98^\circ C.$, and is completely fused at $104^\circ C$. (uncorrected). Dissolves readily in water and alcohol.

Reducing Action upon the Haloid Salts of Silver.

It was thought that the best way to test this question would be to submit some exposed gelatin dry plates to the action of the hydrochinon monosulpho-acid. For this purpose a preliminary test was made, using an Eatman lantern slide-plate, and a solution of the barium salt of the hydrochinon sulpho-acid, made slightly alkaline with sodium carbonate. A positive of very fair quality was thus obtained, the tone of colour being reddish brown. It developed up very slowly, however, but it is expected that better results will be obtained when using a developer of definite composition.

In conclusion I would state that I hope soon to complete experiments upon this subject, and will then submit such further results as I may have obtained.—*Journal of the American Chemical Society*, xiii., p. 155.

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION OF GREAT BRITAIN.
Weekly Evening Meeting, Friday, June 12th, 1891.

SIR FREDERICK BRAMWELL, Bart., D.C.L., F.R.S.,
Hon. Secretary and Vice-President, in the Chair.

"*The Rate of Explosions in Gases.*" By HAROLD B. DIXON, M.A., F.R.S., Professor of Chemistry in the Owens College, Manchester.

The rapid act of chemical change which follows the kindling of an explosive mixture of gases has of late years attracted the interest both of practical engineers and of theoretical chemists. To utilise for motive power the expansive force of ignited gases; to minimise the chance of disastrous confagurations of fire-damp in coal-mines; to follow the progress of chemical changes under the simplest conditions, are some among the problems presented to us in industry or science, demanding for their solution a knowledge of the phenomena of the explosions of gases.

To understand the nature of explosions in gases it is necessary to know certain fundamental properties of the explosive mixture. With this object in view experimenters have sought to determine for various mixtures of gases,—the heat of chemical combination, the temperature of inflammation, the pressure developed, and, lastly, the rate

at which the explosion is propagated under different conditions.

It is on the last of these problems—the determination of the velocity with which the flame travels through the gas—that I have been asked to speak.

Twenty-four years ago Bunsen described a method of measuring the rapidity of the flame in gas explosions. Passing a mixture of explosive gases through an orifice at the end of a tube, and igniting the gases as they issued into the air, he determined the rate at which the gases must be driven through the tube to prevent the flame passing back through the opening and exploding inside the tube. By this method he found that the rate of propagation of the ignition of hydrogen and oxygen was 34 metres per second, while the rate of ignition of carbonic oxide and oxygen was less than 1 metre per second. Bunsen applied these results to the rate of explosion of gases in closed vessels, and his results were accepted without cavil for fourteen years.

By 1880 facts began to accumulate which seemed inconsistent with Bunsen's conclusions. For instance, between 1876-80 I had several times observed that the flame of carbonic oxide and oxygen travelled in a long eudiometer too quickly to be followed by the eye. Mr. A. V. Harcourt, in his investigation of an explosion which happened in a large gas main near the Tottenham Court Road in 1880, was led to the conclusion that the flame travelled at a rate exceeding 100 yards per second. In the winter of 1880-1 I noticed the rapid increase of velocity as a flame of carbon bisulphide with nitric oxide travelled down a long glass vessel; and shortly afterwards I attempted to measure the rate of explosion of carbonic oxide and oxygen by photographing on a moving plate the flash at the beginning and end of a long tube. The two flashes appeared to be simultaneous to the eye, but no record of the rate was obtained, for the apparatus was broken to pieces by the violence of the explosion.

In July, 1881, two papers appeared in the *Comptes Rendus*, one by M. Berthelot, the other by MM. Mallard and Le Chatelier. Both papers announced the discovery of the enormous velocity of explosion of gaseous mixtures. Other papers quickly followed by the same authors. M. Berthelot made the important discovery that the rate of explosion rapidly increases from its point of origin until it reaches a maximum which remains constant, however long the column of gases may be. This maximum M. Berthelot states to be independent of the pressure of the gases, of the material of the tube, and of its diameter above a small limit. The rate of explosion thus forms a new physico-chemical constant, having important theoretical and practical bearings. The name "L'Onde Explosive" is given by Berthelot to the flame when propagated through an explosive mixture of gases at the maximum velocity.

While Berthelot, associated with Vieille, was measuring the rate of the "explosion-wave" for various mixtures of gases, Mallard and Le Chatelier continued the study of the preliminary phenomena of explosion which precede the formation of the "wave." They showed, by photographing on a revolving cylinder,—(1) that when a mixture such as nitric oxide and carbon bisulphide is ignited at the open end of a tube, the flame travels a certain distance (depending on the diameter and length of the tube) at a uniform velocity; (2) that at a certain point in the tube vibrations are set up which alter the character of the flame, and that these vibrations become more intense, the flame swinging backwards and forwards, with oscillations of increasing amplitude; and (3) that the flame either goes out altogether, or that the rest of the gas detonates with extreme velocity. Again, when a mixture of gases was fired near the closed end of the tube, they found the velocity of the flame regularly increased, as far as their instruments were able to record the rapidly increasing pace.

Mixtures of coal-gas with air, and of fire-damp with air, show phenomena of the first and second kind.

Ignited at the open end of a tube, these mixtures burn at a uniform rate for a certain distance, and then the flame begins to vibrate.

The vibrations acquire greater or less velocity according to the nature of the mixture and the conditions of the experiment; but the third *régime* of uniform maximum velocity is not set up. In narrow tubes the explosion soon dies out.

The phenomena studied by Mallard and Le Chatelier have been observed on a large scale in explosions in coal mines. It has been noticed that little damage was caused at the source of an explosion, and for a distance varying from 50 to 80 yards from the origin of the flame, while beyond that distance fall of roof, broken tubs, and blown-out stoppings have testified to the violence exerted by the explosion. Great as the destruction is which an explosion of fire-damp and air causes in a mine, it is fortunate that these mixtures do not *detonate*.

Passing on to Berthelot's researches on the *régime* of detonation, I will briefly summarise the results he has arrived at.

The actual velocities of explosion are compared by Berthelot with the mean velocity of translation of the gaseous products of combustion, supposing these products to contain all the heat that is developed in the reaction.

For instance, we know the total heat given out when hydrogen and oxygen combine. If this heat is contained in the steam produced, we can calculate what its temperature must be if we know its heat capacity. And if we know the temperature of the steam, we can calculate the mean velocity with which the molecules must be moving. Now Berthelot supposes that the heat is all contained in the steam produced. He assumes that the heat capacity of steam is the same as the sum of those of its constituents; and he supposes, moreover, that the steam is heated at constant pressure. Making these assumptions, he calculates out the theoretical mean velocity of the products of combustion of various mixtures, and finds a close accordance between these numbers and the explosion rates of the same mixtures. He concludes that the explosive wave is propagated by the impact of the products of combustion of one layer upon the unburnt gases in the next layer, and so on to the end of the tube at the rate of movement of the products of combustion themselves. If his theory is true, it accounts not only for the extreme rapidity of explosion of gaseous mixtures, and gives us the means of calculating the maximum velocity obtainable with any mixture of gases, but it also affords us information on the specific heats of

TABLE I.
BERTHELOT'S EXPERIMENTS.

Gaseous mixture.	Velocity in Metres per Second.	
	Theoretical	Found.
H ₂ + O		
Hydrogen and oxygen.	2830	2810
H ₂ + N ₂ O		
Hydrogen and nitrous oxide.	2250	2284
CO + O		
Carbonic oxide and oxygen.	1940	1090
CO + N ₂ O		
Carbonic oxide and nitrous oxide.	1897	1106
CH ₄ + O ₂		
Marsh gas and oxygen.	2427	2287
C ₂ H ₄ + O ₂		
Ethylene and oxygen.	2517	2210
C ₂ N ₂ + O ₂		
Cyanogen and oxygen.	2490	2195
C ₂ H ₂ + O ₂		
Acetylene and oxygen.	2660	2482
CO + H ₂ + O ₂		
Carbonic oxide, hydrogen, & oxygen.	2236	2068

gases at very high temperatures, and it explains the phenomena of detonation, whether of gases or of solid or liquid explosives.

Table I. shows the explosion rates found by Berthelot, compared with the theoretical velocity of the products of combustion.

Two points in Table I. favoured the view that Berthelot might have here given the true theory of explosions: first, the close coincidence between the rates of explosion of hydrogen, both with oxygen and nitrous oxide, with the calculated mean velocities of the products of combustion; and secondly, the great discordance between the found and calculated rates for carbonic oxide with both oxygen and nitrous oxide. I had previously discovered that pure carbonic oxide cannot be exploded either with pure oxygen or pure nitrous oxide. The discordance found by Berthelot was what I should have expected from my own experiments.

A consideration of Berthelot's results, published in full in the *Annales de Chemie*, led me to think it would be useful to repeat and extend these experiments. My objects were chiefly—(1) to determine as accurately as possible the rate of the explosion-wave for some well-known mixtures; (2) to measure the rate of the explosion-wave in carbonic oxide with different quantities of steam; and (3) to determine the influence of inert gases on the propagation of the wave.

1. The results obtained with hydrogen and oxygen, with hydrogen and nitrous oxide, and with marsh gas and oxygen, in exact proportions for complete combustion, were in close accordance with the mean results of Berthelot; for ethylene, acetylene, and cyanogen my numbers differed appreciably, but in no case differed by more than 7 per cent from the rates observed by Berthelot:—

TABLE II.

VELOCITY OF EXPLOSION IN METRES PER SECOND.

	Berthelot.	Dixon.
Hydrogen and oxygen, H_2+O	2810	2821
Hydrogen and nitrous oxide, H_2+N_2O	2284	2305
Marsh gas and oxygen, CH_4+O_2 ..	2287	2322
Ethylene and oxygen, $C_2H_4+O_2$..	2210	2364
Acetylene and oxygen, $C_2H_2+O_2$..	2482	2391
Cyanogen and oxygen, $C_2N_2+O_2$..	2195	2321

The general agreement between these measurements left no room for doubt about the substantial accuracy of Berthelot's experiments. The formula he gives does therefore express, with a close degree of approximation, the rates of explosion of many gaseous mixtures.

2. The formula fails for the explosion of carbonic oxide with oxygen or nitrous oxide. This was to be expected if—in the detonation of carbonic oxide in a long tube—the oxidation is effected indirectly by means of steam, as it is in the ordinary combustion of the gas. Measurements of the rate of explosion of carbonic oxide and oxygen in a long tube showed that the rate increased as steam was added to the dry mixture, until a maximum velocity was attained when between 5 and 6 per cent of steam was present.

3. When electrolytic gas was mixed with an excess of either hydrogen or oxygen the rate of explosion was found to be altered; the addition of hydrogen increasing the velocity, the addition of oxygen diminishing it. The addition of an inert gas, nitrogen, incapable of taking part in the chemical change, produced the same effect as the addition of oxygen,—one of the reacting substances.—only the retarding effect of nitrogen was less marked than that of an equal volume of oxygen. The retardation of the explosion-wave caused by the addition of an inert gas to electrolytic gas evidently therefore depends upon the volume and the density of the gas added. In the following table the retarding effect of oxygen and nitrogen, on the explosion of electrolytic gas, is compared:—

TABLE III.

RATE OF EXPLOSION OF ELECTROLYTIC GAS WITH EXCESS OF OXYGEN AND NITROGEN.

Volume of oxygen added to H_2+O	O_2	O_3	O_5	O_7
Rate	2328	1927	1690	1281
Volume of nitrogen added to H_2+O	N_2	N_3	N_5	N_7
Rate	2426	2055	1822	—

I think it a fair inference from these facts to conclude, when the addition of a gas to an explosive mixture retards the rate of explosion by an amount proportional to its volume and density, that such added gas is inert as far as the propagation of the wave is concerned, and that any change which it may undergo takes place after the wave-front has passed by—in other words, is a *secondary* change.

This principle has been applied to determine whether, in the combustion of gaseous carbon, the oxidation to carbonic acid is effected in one or two stages—an important question, on which there is little experimental evidence. If, for instance, in the combustion of a hydrocarbon, or of cyanogen, the carbon is first burnt to carbonic oxide, which subsequently is burnt to carbonic acid, the rate of the explosion-wave should correspond with the carbonic oxide reaction, in this case the primary reaction; whereas, if the carbon of these gases burns to carbonic acid directly, in one stage, then the rate of the explosion-wave should correspond with the complete reaction.

Now, if we adopt Berthelot's formula as a working hypothesis, we can calculate the theoretical rates of explosion of marsh gas, ethylene, or cyanogen:—(1) on the supposition that the carbon burns directly to CO_2 , and (2) on the supposition that the carbon burns first to CO , and the further oxidation is a subsequent or secondary reaction. On the first supposition, if 100 represents the rate of explosion of these three gases burning to carbonic oxide, the addition of the oxygen required to burn the gases to carbonic acid should *increase* the rate of explosion:—

	Marsh Gas.	Ethylene.	Cyanogen.
Calculated rate of explosion when burnt to CO_2	104	103	107

Whereas if these gases really burn first to carbonic oxide, and the extra oxygen is inert in propagating the explosion-wave, then the addition of this inert oxygen would diminish the rate of explosion:—

	Marsh Gas.	Ethylene.	Cyanogen.
Calculated rate of explosion when burnt to CO with inert oxygen present ..	92	88	87

The experiments show that if 100 be taken as the rate of explosion when the oxygen is only sufficient to burn the carbon to carbonic oxide, the following are the rates found when oxygen is added sufficient to burn the carbon to carbonic acid.

	Marsh Gas.	Ethylene.	Cyanogen
Rates found	94	92	84

The results are therefore in favour of the view that, in the explosion of these gases, the carbon is first burnt to carbonic oxide.

But stronger evidence on this point is obtained by comparing the explosion rate of these gases (1) when fired with oxygen sufficient to burn the carbon in them to carbonic acid, and (2) when nitrogen is substituted for the oxygen in excess of that required to burn the carbon to carbonic oxide. We have seen that oxygen added to electrolytic gas hinders the explosion more than nitrogen. In precisely the same way oxygen added to a mixture of equal volumes of cyanogen and oxygen hinders the ex-

plosion more than the same volume of nitrogen. The conclusion we must come to is that the oxygen added to the mixture expressed by the formula $C_2N_2 + O_2$ is as inert (so far as the propagation of the explosion-wave is concerned) as oxygen added to the mixture expressed by the formula $H_2 + O$. The same phenomena occur in the explosion of marsh gas, ethylene, and acetylene. In all these cases the substitution of nitrogen for the oxygen required to burn the carbon from carbonic oxide to carbonic acid *increases* the velocity of the explosion. These facts seem only consistent with the view that the carbon burns directly to carbonic oxide, and the formation of carbonic acid is an after-occurrence.

Finally, the rates of explosion of cyanogen and the hydrocarbons, when their carbon is burnt to carbonic oxide, have been found greater than the velocities calculated from Berthelot's formula. This accords with the observation previously made that the rate of explosion of electrolytic gas with excess either of hydrogen or oxygen is far higher than the calculated rate. It would seem probable that the theoretical rates as calculated by Berthelot should be modified, in spite of the close agreement which his numbers show. I think the low rates found, when hydrogen, marsh gas, cyanogen, &c., are exploded with equivalent proportions of oxygen, depend partly on the carbon burning to carbonic oxide, and partly on the dissociation of the steam at the high temperature. If the formula is modified in these respects, velocities can be calculated which agree with the experimental results where dissociation does not occur. I suggest the following modifications:—(1) the specific heats should be taken at constant volume instead of at constant pressure; (2) the density of the gas should be taken as the mean of the burnt and the unburnt molecules, instead of that of the burnt molecules alone; and (3) a correction should be made for the alteration of volume by the chemical reaction, which in some cases increases, in others diminishes, the volume.

The rates so calculated agree with the explosion rates of cyanogen when burnt to carbonic oxide either by oxygen, nitrous oxide, or nitric oxide; with the explosion rates of hydrogen and oxygen with a large excess either of hydrogen, oxygen, or nitrogen; with the explosion rates of ethylene and acetylene with oxygen and a large excess of nitrogen; and, lastly, with the explosion rates of hydrogen and chlorine with an excess of hydrogen.

In conclusion, I would say that these experiments have amply confirmed the truth of Berthelot's statement that the explosion-wave is a "specific constant" for every gaseous mixture; that it has been shown that the rate of explosion depends upon the primary reaction occurring, and that the determination of the rate may throw some light on what is now so obscure—the mode in which chemical changes are brought about; and, finally, that it does not seem impossible that a connection between the rate of the molecules and the rate of the explosion may be worked out, which will give us some definite information on points of high interest in the theory of gases.

CORRESPONDENCE.

ESTIMATION OF ALUMINIUM IN IRON AND STEEL.

To the Editor of the Chemical News.

SIR,—Mr. A. S. Blackley has drawn attention to a method for the determination of aluminium in iron and steel described by me before the Society of Chemical Industry, Dec. 31, 1889, and also described by M. Carnot in your journal, pointing out that M. Carnot's method is substantially the same as mine. Practically speaking, they are identical.

I have, however, quite recently learned that although M. Carnot has never before made public his method, he claims to have taught it to his pupils for many years.

Let me point out that at the time I read my paper there was no simple method, so far as I could learn, published for the determination of minute quantities of aluminium in steel, and I explained that the process I described was simply a combination of several already well-known methods.

It gives me very great pleasure to find that other chemists, who have quite independently worked with the same object in view, should have confirmed each other. We may conclude, therefore, that the best method for determining small amounts of aluminium in steel is that described by M. Carnot and myself.—I am, &c.,

J. E. STEAD.

Laboratory and Assay Office,
5, Zetland Road, Middlesbrough,
July 30, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 3, July 20, 1891.

The Composition of Atmospheric Air. New Method in Weight.—A. Leduc.—the author, taking account of the relative results for the weight of a litre of air obtained by Regnault and by himself, is led to conclude that the variation in time of the weight of atmospheric air extends at most to the ten-thousandths.

On Silicon Selenide.—Paul Sabatier.—The author has obtained this compound by heating to redness crystalline silicon in a current of hydrogen selenide perfectly dry. The transformation takes place without appreciable incandescence at a temperature a little higher than the boiling-point of selenium. The selenide obtained has the form of a melted mass, hard, iridescent, of an aspect almost metallic, and does not appear to be volatile at the temperature of the experiment. Its composition is represented by the formula $SiSe_2$. Its properties resemble those of boron selenide, but being more compact it reacts much more slowly with destructive agents. Water acts very briskly, producing silica and hydrogen selenide. The total destruction of the selenide is never effected, even by prolonged immersion in hot water. Potassa produces a complete decomposition, dissolving both silica and hydrogen selenide, though a considerable time is required. Aqua regia attacks silicon selenide regularly; gelatinous silica is formed, and there remains a slight residue of silica which escapes the reaction. Silicon selenide exhales a very irritating odour, due to hydrogen selenide, formed by the moisture of the air acting upon its surface. If it is heated to dull redness in a current of dry air or oxygen, it is oxidised, forming selenious anhydride and selenium. But the combustion is only superficial.

Melting-Point of Certain Binary Organic Systems (Hydrogen Carbides).—Leo Vignon.—If we have a mixture of two definite substances, solid and fusible, not reacting chemically upon each other, in the ordinary sense of the word, and determine their melting-point, we find that it generally differs from the mean of the melting-point of the component bodies. This fact has been observed with mixtures of metals, of fusible salts, and fatty acids. The author has verified the same phenomenon in experimenting on mixtures of hydrocarbons, phenols, amines, and anhydrides, which have a melting-point, ϕ , differing from the mean, F , of the melting-points of their components.

Study of the Solid Products resulting from the Oxidation of the Drying Oils.—Ach. Livache.—When the drying oils, whether raw or having undergone an appropriate treatment, have taken up all the oxygen which they are capable of absorbing, they are found converted into a solid elastic mass, perfectly dry, and of a colour more or less brown according to the method of preparation. There is a close analogy from the physical point of view between the product of the oxidation of drying oils and caoutchouc. The author points out the prospective industrial applications of this product.

New Method of Determining Phenol.—L. Carré.—The author weighs 10 grms. of pure phenic acid, and makes up its solution to 1 litre, and with this he prepares a series of standard liquids progressively weaker at 5, 4, 3, 2, 1 grm., 0.8, 0.6, 0.4, 0.2, 0.1 grm. per litre. Suppose a solution of phenic acid. If it is concentrated it is first diluted to $\frac{1}{10}$ th. Of the dilute liquid 25 c.c. are taken and introduced into a flat-bottomed flask with 5 c.c. of nitric acid. Similar portions are taken from the standard solutions, and all the flasks are placed on one and the same water-bath for one or two hours after each has received an equal admixture of nitric acid. All must be heated for exactly the same length of time. Under these conditions there are produced nitro-phenols in proportions which depend evidently on the respective quantities of the elements coming in contact. The colouration found in two experiments having the same concentration of phenol, heated for the same time and in the same manner, is always strictly equal. A preliminary examination will permit us to eliminate the standards, the colouration of which deviates too far from that of the sample under examination. To obtain further precision after the action of nitric acid at the temperature of the water-bath we add 20 c.c. of caustic soda and make up the volume to 50 c.c. We filter, if necessary, and compare the specimen with the standard which approaches nearest to it in shade with the aid of the colorimeter. The author has thus found 3.52 grms. and 0.09 grm. phenol per litre, the real quantities being 3.50 and 0.10 grm. If alcohol is present it must be driven off. Impure phenols must be heated long enough to destroy the tarry products present.

On Ozone considered from a Physiological and Therapeutic Point of View.—D. Labbé and M. Oudin.—If ozone is prepared by the chemical method it is always impure, being accompanied by highly poisonous compounds, e.g., phosphorous acid. If it is prepared from pure oxygen there are obtained considerable quantities, which, being mixed with unconverted oxygen, constitute a total necessarily dangerous to breathe in a confined space. If animals are allowed to breathe in an uninclosed space, a mixture of atmospheric air and ozone, no accidents occur. Hence ozone is not dangerous to respire.

The Action of the Butyric Ferment in the Transformation of Starch into Dextrine.—A. Villiers.—The butyric ferment secretes a soluble product capable of effecting the conversion in question in the absence of any organised ferment. This product seems to be formed continuously in small proportions, and its action is rapidly exhausted as it is elaborated.

MISCELLANEOUS.

International Congress of Hygiene and Demography.—The following are the chief papers which will be read in Section V., Chemistry and Physics:—

Tuesday, August 11th.—"Town Fog and its Effects," including Smoke Prevention, introduced by Dr. W. J. Russell, F.R.S.; "On the Air of Large Towns and Methods of its Analysis," by the Manchester Field Naturalists' Society, Town Gardening Section; "The Means at our Disposal for Preventing the Emission of

Smoke from Factories and Dwelling-houses," by Mr. A. E. Fletcher, H.M. Chief Inspector of Alkali Works. Dr. C. Theodore Williams will take part in the discussion with regard to Fog in Relation to Health."

Wednesday, August 12th.—"Treatment of London Sewage," by Dr. Dupré; "Outline of the Various Chemical Processes for Filtering Sewage," by Dr. J. C. Thresh; "The Duty of a Locality to Utilise the Nitrogen of its Sewage for the Benefit of the Nation," by Dr. Alfred Carpenter; "The Power of Soil and Vegetation Combined to Destroy Disease Germs, and so Prevent the Possibility of the Spread of Enthetic Disease in consequence of Sewage Farming," by Dr. Alfred Carpenter. Herr Stadtrath Marggraf, of Berlin, also promises a paper if unable to be present and take part in the discussion.

Thursday, August 13th.—"The Hygienic Importance of Copper," by Prof. Dr. Lehmann, of Würzburg; "The Importance to be Attached to Magnesia in Drinking Water," by Prof. P. F. Frankland, F.R.S.; "The Action of Water on Lead," by Dr. J. H. Garrett; "The Antiseptic Treatment of Food," by Mr. Otto Hehner; "The Effects of the Respiration of Carbonic Acid on Man," by Dr. W. Marcet, F.R.S.

Friday, August 14th.—"The Influenza and Weather of London," by Sir Arthur Mitchell and Dr. A. Buchan; "Hygienic Improvements in the Manufacture of Bread," by Mr. J. Goodfellow, F.R.M.S. It is hoped that papers will also be contributed by Prof. Dr. O. Liebreich, of Berlin, and Prof. Dr. G. Lunge, of Zurich.

Recognition of a Fraudulent Addition of "Rubenkraut" in Rhenish Obst-Kraut.—The article known on the Rhine as "Obst-Kraut," and in Eastern Germany as Obstmuss, consists of apples, pears, or plums boiled down to a paste without the addition of sugar. It is apparently sophisticated with "Rubenkraut," a concoction of turnips.—*Zeitschrift*, xxix., Part 6.

Orsat's Apparatus for the Analysis of Chimney Gases.—This apparatus, both in its original form and in its ordinary modification, has the defect that the absorbent vessels filled with the capillary tubes is very fragile, and that the introduction and removal of these tubes is very tedious. Greiner and Friedrichs (*Zeit. Angew. Chemie*) propose a modification to obviate this defect. John Ruffle and James Mac Lachlan (*Jour. Soc. Chem. Ind.*) propose further improvements.

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THE CHEMICAL NEWS.

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NOTE UPON THE POWERFUL REDUCING ACTION OF SILICON.

By H. N. WARREN, Research Analyst.

METALLIC, or graphitoidal, silicon is in itself one of the most stable and inert substances with which specialists are acquainted, refusing even the oxidising influence of the oxyhydrogen flame, but strange to say that this substance, when in admixture with a large number of metallic oxides, becomes at once oxidised, the oxide in admixture with the same becoming itself reduced. Thus, for instance, if an excess of litharge be heated to dull redness only, in contact with silicon, it becomes at once reduced to metallic lead; and, with the same facility as if carbon had been employed, when an excess of silicon is introduced a brittle regulus of silicide of lead is produced, although no such compound is obtained when these elements are heated together. With copper, and all readily reducible oxides, either a silicide or—when the oxide is in excess—the pure metal is obtained. A curious compound is obtained when a slight excess of silicon and oxide of silver are projected into a red-hot crucible; incandescence takes place with considerable brilliance, the product formed being a semi-fluid compound, containing about 40 per cent of silicon, in appearance resembling cupric sulphide, but, unlike that substance, refusing to melt at the highest furnace temperatures, and only with difficulty when before the flame of the oxyhydrogen blowpipe.

Even metallic chromium is readily reduced by heating silicon together with the oxide of that metal, tungstic and molybdic oxides suffering a like decomposition.

A mixture of equal parts of finely-divided silicon, aluminum, and litharge, when heated together, explode with fearful violence; in fact, so powerful is the explosive strain that I have failed to obtain any article to withstand it, which must be equal, if not superior, to fulminating silver, even cast-iron being readily shattered. The experiment is most safely performed by taking not more of the mixture than would cover a threepenny piece, supporting the same upon a stout clay-brick, and directing the flame from the blowpipe upon it: the whole generally very quickly melts, then frequently assumes a spherical condition similar to a globule of sodium. At this point it disappears with a deafening report, producing a vivid flash of light accompanied by a large volume of vapour. The surface of the brick, after the experiment, is observed to have become indented, similar to the effects observed from the detonation of nitrogen chloride.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

CONTRIBUTIONS TO THE CHEMISTRY OF ERBIUM AND DIDYMIUM.*

By GERHARD KRÜSS.

(Continued from p. 66).

In this manner there were obtained six fractions of double sulphates, which were separately converted into nitrates by the repeated precipitation of their solutions with ammonia, by re-dissolving the precipitates (at first basic sulphates and afterwards hydroxides) in nitric acid. The absorption spectra were figured according to careful

measurements made with a universal spectral apparatus adjusted for wave-lengths.

It appeared, as might be expected, that the didymium was strongly accumulated in the first fractions; and that in the last fraction the double band D_{17} at $\lambda = 579.2$ and 575.4 , so characteristic of didymium, are entirely wanting. In none of the fractions were the didymium lines observed without the simultaneous presence of the erbium lines, E_{18} at $\lambda = 654.7$ was always visible, and in this manner similar results were obtained to those observed according to the method recommended (Mosander and Bunsen).

If, in separating didymium oxide from erbia, we wish to set out from the different basicity of these oxides, we may most advantageously either decompose the mixed nitrates fractionally by cautious heating, or the solution of the mixed oxides may be partially precipitated, e.g., with ammonia. The former process ranks amongst the methods most commonly used in the separation of mixed earths. Whoever has undertaken the troublesome task of decomposing considerable quantities of the nitrates by several hundreds of fractionated heatings knows how tedious is this method, and how oppressive it becomes by the continual escape of nitrous vapours.

Fractionation of the Mixed Earths with Ammonia.—It should therefore be attempted to decompose the raw material of rare earths, as obtained directly from the minerals, as far as possible by a fractionated precipitation of the neutral solution of the nitrates with very dilute ammonia. In principle such a fractionated separation of the earths from their solutions by means of ammonia is not novel; it has been used by Cleve, Crookes, Lecoq de Boisbaudran, and others, but always merely to test the homogeneity of an earth obtained in some other manner.

Fractionation with ammonia has, in so far, the advantage over the partial decomposition of the nitrates by heat, as it furnishes in the precipitates the several earths more correctly in the serial order of their basicity. In the fractional decomposition of the earthy nitrates by heat, even if the operation is conducted in baths of known temperatures, it is difficult to keep large portions of the nitrates, when fused to pasty masses, at a uniform temperature throughout. Single portions of such melts, which come most in contact with the air, on stirring deposit themselves in crusts on the edges of the capsule and on the spatula, whilst others become more strongly heated against the sides of the capsule. On the other hand, a dilute solution of an earthy nitrate can be quickly and completely mixed with very dilute ammonia *before* a precipitation takes place, as in dilute solutions a gradual turbidity ensues only after some time, followed by the deposition of hydroxide.

Five kilos. of selected gadolinites, from Hitteroe or Ytterby, which I obtained directly from Sweden, thanks to the kindness of Herr Nilson, were ground very finely in a mill, and decomposed with hydrochloric acid by heating in large capsules. The large part of the earths present passed into solution on the first treatment with acid, whilst a small portion remained in the insoluble residue even after a second treatment with hydrochloric acid. The latter was therefore repeatedly fused with potassium hydrosulphate, the melts were treated with much water, and thus almost all the earths of the gadolinites were ultimately brought into solution. The rare earths were first precipitated from the acid solution by means of oxalic acid, and, as the supernatant solution was rich in iron, the precipitated oxalates were frequently boiled with hydrochloric acid. After drying and ignition the oxalates yielded rather more than a kilo. of the mixed rare earths.

The yellowish white oxide was completely soluble in nitric acid, and on evaporating the solution of the nitrates there was first separated out a not inconsiderable quantity of basic salts of iron and cerium, which were filtered off. The filtrate was then evaporated down several times, the residue being always taken up with water. Thus there was obtained an almost neutral solution of the

* Liebig's Annalen.

mixed earthy nitrates which was to be submitted to fractionated precipitation with ammonia. The absorption-spectrum of this initial solution was first closely examined with the universal spectroscope described by the author (*Ber. Deutsch. Chem. Gesell.*, xix., p. 2739), and the several lines were laid down in tables according to their relative intensities and the wave-lengths of their maximum darkness.

The fractionated precipitation was then carried out as follows:—To the solution of nitrate, previously diluted to about 20 litres, there were added at once, and with most vigorous stirring, 100 c.c. ammonia of sp. gr. 0.91, previously diluted with 2 litres water. The precipitate gradually formed settled well, and could be washed by decantation. It was filtered, and finely washed on the filters until ammonia ceased to produce a precipitate in the filtrate. Meanwhile the filtrates were again concentrated to about 20 litres, and were again fractionally precipitated with ammonia. In this manner ten fractions were obtained from the material, the neutral nitrate solutions of which yielded ten spectra. The first three fractions had nearly identical spectra, as also the fourth and fifth. Hence the erbium was accumulated in the first fractions, whilst in the spectrum of the last precipitates the erbium lines $\text{Er}\alpha$ ($\lambda=654.7$) and $\text{Er}\beta$ ($\lambda=523.1$) were entirely wanting, and, with the exception of a few thulium, holmium, and samarium lines, only those of didymium were present.

A second series of fractionated precipitations was then carried out with ammonia in dilute solutions, and there were obtained from the fractions—

1—3	..	..	..	..	11—18
4—5	..	..	..	..	19—25
6	..	..	..	..	26—31
7	..	..	..	..	32—35
8	..	..	..	..	36—40
9	..	..	..	..	41—46

The decomposition of the fraction of the first series was effected simultaneously, so that the fractions 11 to 46 were obtained in a relatively short time. Their absorption spectra showed that the first fractions of every new series were the richest in erbium, and that didymium passes more and more into the last precipitates of each series. Fraction 10 of the first series, when anew resolved by ammonia into five parts, gave fractions which were identical in their spectra.

It appears that, in order to undertake a third series of fractionated precipitations with ammonia, it is most advantageous to unite the fractions—

11—14, 19—21, 26—28, 32, for a material rich in erbium.

15, 16, 22, 23, 33, and 36, for a mean fraction No. 1.

17, 24, 29, 30, 34, 37, and 38, for a mean fraction No. 2.

10, 18, 25, 31, 35, 39—46, for a material rich in didymium.

The mean fractions Nos. 1 and 2 were first fractionated, the first precipitates being then mixed with the material rich in erbium, and the last precipitates with the material rich in didymium. The last two main portions were resolved by ammonia into a third series of fractionated precipitates, and so there was obtained a didymium material the most concentrated nitrate solution of which, even in a stratum 15 c.m. in thickness, no longer displayed any erbium bands in its absorption spectrum. The erbium material obtained at the same time had to be submitted to a fourth fractionation with ammonia in a very dilute solution, and the nitrate now obtained showed the erbium bands very intensely; but even in a stratum of 15 c.m. in thickness (solution of 300 grms. nitrate in 150 c.c. water) not a trace of the otherwise so intense didymium band at $\lambda=579.2$ and $\lambda=575.4$.

Such erbium and didymium materials can be obtained in a relatively very short time, as ten or more precipitates

can be obtained and worked up simultaneously. The condition for full and rapid success is washing out the ammoniacal precipitates, as thoroughly as possible, by decantation in water.

The earths obtained in this manner are still contaminated by colourless oxides, and, as the earths of ammoniacal fractionation are chiefly grouped according to basicity, didymium is chiefly accompanied by lanthanum, samarium, yttrium, and terbium, whilst erbium is chiefly accompanied by holmium, thulium, scandium, ytterbium, and cerium, provided that all these rare elements are present in the raw materials employed.

A moderately complete separation of the colourless earths of erbium and didymium was carried out *without* employing the common method of a fractionated decomposition of the nitrates of heat.

To obtain a pure didymium the following method was adopted by Dr. K. Bröckelmann (Inaugural Dissertation, Erlangen, 1891). *Beiträge zur Kenntniss der Elemente der Yttrium und Cer. Gruppen.*

In order to eliminate small quantities of cerium which still accompanied the didymium, the solution of the nitrate was mixed with a large excess of soda-lye and treated with chlorine. The hydroxides of didymium, lanthanum, and those of the colourless earths, were dissolved, whilst the residual cerium hydroxide retained but little didymium. After removing the cerium and expelling the chlorine from the filtrate, it was precipitated with ammonia, and the earthy hydrates—after being well washed—were converted into nitrates. The solution thus obtained did not give the reactions of cerium.

Hereupon the solution of didymium, almost neutral, was caused to crystallise with an excess of potassium sulphate. The rose-coloured crystalline crusts formed contained, along with didymium, a little samarium, and possibly scandium and lanthanum.

In the solution there were traces of samarium, and further of yttrium, and, if present, erbium, terbium, and ytterbium. The solution was drained away from the double sulphate by means of a filter-pump, the crystals were washed with a saturated solution of potassium sulphate, and from all the filtrates colourless hydroxide was obtained by repeated treatment with ammonia, and converted into nitric solution. The solution thus obtained displayed in its spectrum very faint samarium lines, and contained chiefly—

Yttrium (atomic weight = about 90).

Ytterbium (atomic weight = 172).

Terbium (atomic weight = about 300).

For further examination the oxide present on solution was carefully purified for the determination of its atomic weight, and on conversion into anhydrous sulphate it contained a—

$$\frac{\text{III}}{\text{R}} = 99.9.$$

(To be continued).

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 65).

XVII.—Barium.

1. WITH sulphuric acid. Barium sulphate dissolves in hot concentrated sulphuric acid; it crystallises on evaporation, and cooling in rectangles of 5—12 micro., and in X-shaped skeleton crystals with right extinction. An admixture with strontium may impress upon the crystals the form of strontium sulphate (see Strontium). Limit of the reaction, 0.60005 m.grm. Ba.

Ferric chloride retards the precipitation by sulphuric

* *Zeit. Anal. Chem.*

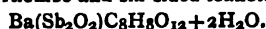
acid. If much ferric chloride and hydrochloric acid are present, there are formed rhombs of 20—50 micro. with rounded angles. Chromium and aluminium chlorides have a similar effect.

2. With fluosilicates. Instead of silico-fluoric acid, as recommended by Bovicky, there may be used ammonium fluosilicate. Not too small a quantity of the reagent and of acetic acid must be used. A slow precipitation yields prisms with a dome of 40—70 micro.; rapid precipitation produces oval leaflets and thorny globules. Strontium and calcium are not precipitated. Limit of the reaction, 0.00009 m.grm. Ba.

3. With potassium bichromate. Light yellow squares and rectangles of 10—20 micro., easily distinguished from strontium carbonate by their form. Calcium is not precipitated. Limit of the reaction, 0.00008 m.grm. Ba.

The barium solution is mixed with sodium or ammonium acetate and a sufficiency of acetic acid. Complete precipitation requires some time, but it may be accelerated by cautious heating. Compare Strontium.

4. With tartar emetic (proposed by Streng) there are obtained thin rhombs and six-sided leaflets of—



The reagent must be added to the hot solution, which should be neutral or faintly acidulated with acetic acid. Limit of the reaction, 0.00045 m.grm. Ba.

Potassium ferrocyanide, used in the same manner, gives, according to Streng, pale yellow rhombic octahedra, characteristic for barium. But calcium is precipitated by the same reagent.

Oxalic acid in presence of nitric acid throws down strontium and calcium, whilst barium is precipitated only after prolonged evaporation or the addition of sodium acetate. Boric acid and aluminium and iron chlorides retard and modify the precipitation (compare Iron). The peculiar action of stannic chloride will be considered under Strontium.

Ammonium carbonate precipitates from pure solutions of barium stars of 40 micro. If strontium, calcium, or magnesium is present, the reagent is useless.

XVIII.—Strontium.

1. With sulphuric acid we obtain, by the procedure described under Barium, rhombs and crosses, four times as large as those of barium sulphate. The limit of this reaction is at 0.0002 m.grm. Sr. It is characteristic for strontium, since a mixture of equal parts of barium and strontium sulphates yields exclusively crystals of the form of strontium sulphate. Ferric chloride retards the precipitation. If so much iron is present that the margin of the drops appears strongly yellow during evaporation, there appear globules and rounded cubes of about 10 micro. between rods of 30 micro. Barium sulphate appears subsequently in the above-described rhombs of 20—40 micro.

2. With potassium bichromate. Neutral chromate precipitates neutral solutions of strontium salts immediately. Bichromate gives a precipitate if much sodium acetate is added. The precipitate appears the more tardily the more acetic acid is present; more rapidly if the liquid is heated to 100°. It consists of pale yellow globules of from 20—30, or, under favourable circumstances, 100 micro. It is produced most rapidly by local supersaturation with a drop of ammonia. Limit of the reaction, 0.0008 m.grm. Sr. It is decisive in the absence of zinc.

3. With double potassium and sodium tartrate (Seignette's salt). Massive sharply-developed rhombic crystals, of the form of mispickel, isomorphous with calcium tartrate. Limit of the reaction, 0.0004 m.grm. Sr. Acetic acid retards the reaction but slightly. Barium must be previously removed, as it would carry down the strontium in the form of a powder. Calcium must not be present, as there are otherwise formed mixed crystals. Boric acid, and the aluminium, chromium, and iron chlorides occasion a granular precipitation.

4. Sodium bicarbonate precipitates, at common temperatures, radially fibrous globes, with a zonal structure and fine polarisation cross of 20—25 micro. They have so strong a double refraction that between nicols there appears a system of rings extending to the third order. Limit of the reaction, 0.0004 m.grm. Sr.

Tartar emetic gives the same reaction as barium. Oxalic acid in presence of nitric acid produces finely-developed rhombic crystals of 20—40 micro., and of an octahedral aspect. Unfortunately the reaction of oxalic acid with calcium salts is quite similar. Aluminium, chrome, and iron chlorides have little influence. The action of stannic chloride is very remarkable. If we mix an acid solution of barium, strontium, and calcium with stannic chloride, and add oxalic acid, there is first strontium precipitated in tetragonal, faintly polarising pyramids of 60—100 micro. The gradual neutralisation of the free hydrochloric acid throws down then the barium in the form of six-rayed stars of 50—120 micro., and, lastly, the calcium, which yields insignificant quadratic tables and granules of 10—25 micro. Hitherto only the crystals of the strontium compound have been closely examined. They contained, along with strontium, a considerable quantity of tin. The limit of the action is for strontium 0.0008 m.grm., for barium 0.0005 m.grm., and for calcium 0.00005 m.grm.

(To be continued).

ON SOME LECTURE EXPERIMENTS ILLUSTRATING PROPERTIES OF SALINE SOLUTIONS.*

By Prof. J. G. MACGREGOR, Dalhousie College, Halifax, N.S.

(1). IN a paper printed in the last volume of the *Proc. and Trans. N. S. Inst. Nat. Sci.* (vol. vii., 1889, p. 368), I pointed out that, according to Kohlrausch's observations, sufficiently dilute solutions of sodium hydroxide have volumes which are less than the volumes which their solvent would have in the free state, 1 grm. of a solution containing about 6 per cent of the hydroxide having a volume 0.0045 c.c. less than the water it contains. Several other substances are known which exhibit the phenomenon of contraction on solution in a similarly marked manner, but none which exhibit it to such an extent. This hydroxide, therefore, affords the best means of exhibiting the phenomenon of contraction by a lecture experiment.

The simplest mode of conducting the experiment is to pass the powdered caustic soda, little by little, down a glass tube forming a prolongation of the neck of a large bottle, the bottle and part of the tube having been first filled with distilled (or, indeed, undistilled) water. The substance is quickly dissolved by the water, the strong solution thus formed sinks and mixes with the water below, and the change of volume of the liquid is indicated by the change of height of the column of liquid in the tube. In order that the experiment may be made quickly, the powder must not be allowed to form a cake in the tube where it meets the water. To avoid this, a tube of about 7 or 8 m.m. diameter must be used. It should be several inches in length, and should have the upper end opened out to a funnel shape, to facilitate the introduction of the powder. The tube being necessarily of large bore, the bottle must also be large, so that a small change of volume may be indicated by a comparatively large elevation or depression in the tube. The hydroxide should be in the form of a powder, not only that its solution may be accomplished quickly, but also because the solution formed must be dilute in order to secure a depression of the liquid in the tube. If it be not powdered, the sub-

* From the *Transactions of the Nova Scotian Institute of Science*, Session of 1890-91.

stance falls to the bottom and forms a strong solution there, which only gradually diffuses into the water above. Even with a fine powder, however, a comparatively strong solution is formed at the bottom. Hence I have found it advisable to catch the powder in a wire-gauze cage, attached by sealing-wax to the inner end of the rubber stopper which carries the tube, and to hasten the mixture of the strong solution, formed in the tube and cage, with the water, by diverting the downward currents of the strong solution towards the sides of the bottle by means of a plate of glass hanging horizontally below the cage. If a wide-mouthed bottle be used a stirrer may be introduced through the stopper, but leakage is thereby rendered more probable. The full amount of the contraction indicated by Kohlrausch's observations cannot of course be shown. For (1) the powdered caustic soda already contains a considerable quantity of water; (2), the solution of the substance is attended by a development of heat involving a rise of the liquid in the tube; (3), the powder carries air with it into the water, which must increase the volume whether it dissolves or remains suspended; for in the latter case, if a quick effect is desired, there is not sufficient time for it to escape up the tube; and (4), whatever precautions may be taken to secure a uniform solution throughout the bottle, it cannot be at all completely secured in the time at disposal. But notwithstanding these difficulties the experiment is a very striking one, especially if projected by a lantern on a screen. As the powdered caustic soda is passed down the tube, little by little, the liquid is seen to dissolve it without any increase in bulk, and, if the substance does not already contain too much water, with an actual diminution in bulk, the level of the liquid sinking in the tube. If the powder be added in large quantity there is a sudden rise of liquid in the tube, followed by a gradual shrinkage, which continues until the level of the liquid is lower than at the outset. The amount of the depression of the liquid in the tube is sometimes small, depending apparently upon the amount of water which the powdered caustic soda has already absorbed. The substance should not be too finely powdered, as in that case it is likely both to have taken up a considerable quantity of water and to carry down with it a considerable quantity of air. The experiment requires only a few minutes to perform.

(2). The working hypothesis which I use when thinking of the phenomena of solution has led me to the conclusion that elevation of the temperature of a solution will have, if not identically, at any rate in a general way the same effect on its selective absorption of light, and therefore on its colour, as increase in its concentration. All the experimental evidence of which I can find any record bears out this conclusion. But, whether it holds generally or not, it may be shown, by a striking lecture experiment, to hold in the case of two salts, the chlorides of cobalt (CoCl_2) and iron (FeCl_3). To do so make a trough, for projection with a lantern, having thin glass sides, about the size of a lantern-slide, the glass sides being 1 or 2 m.m. from one another. It may readily be made by cutting a U-shaped piece from a sheet of india-rubber, and cementing the glass plates to its opposite sides. Half fill the trough with a saturated solution of either salt, and fill up with a weak solution. If cobalt chloride have been used, the solution in the lower part of the trough will at ordinary temperatures be of a purplish blue, that in the upper part red; and it will be obvious that increase of the concentration of this salt involves increase of blueness in the transmitted light. If now a Bunsen flame be played carefully over one side of the trough, the solutions rapidly rise in temperature, and both are seen to increase in blueness, the saturated solution becoming deep blue and the weak solution purplish red. If the iron chloride have been used, the solution in the lower part of the trough, before heating, is seen to be of a deep orange colour, that in the upper part yellow: and it is obvious that increase in the concentration of this salt involves increase in redness. If, now, the flame be applied as before, the yellow solution

is at once seen to become orange and the orange solution red. Owing to the narrowness of the trough and the thinness of its glass sides, sufficient heating to produce a marked change of colour occupies only half a minute or so. The same trough may of course be used to project the absorption spectra of these solutions on the screen. If the slit be covered half by the one solution and half by the other, both absorption spectra may be seen at once, side by side, and the gradual variation of the spectra may be watched as the trough is gradually heated.

As a means of showing the variation of the colour or absorption spectrum of a solution with concentration, the above experiment has an obvious defect, viz., that the thickness of the layer of the strong and weak solutions being equal, the numbers of the salt molecules through which any ray of light passes are very different in the two cases. It should therefore be supplemented by showing also the colour or the spectrum obtained when the light is passed through a wide trough of the dilute solution, the ratio of the widths of the troughs being the reciprocal of the ratio of the percentages of salt in the two solutions.

(3). Dr. W. J. Nicol's observation (*Phil. Mag.*, ser. v., vol. xix., 1885, p. 453), that anhydrous sodium sulphate will dissolve in a supersaturated solution of that salt, may readily be shown as a lecture experiment by projection. For that purpose place a test-tube containing the solution in a trough with glass sides full of water, and focus it on the screen. Then let the anhydrous salt, in the form of a fine powder, fall upon the surface of the solution. By taking a pinch of the powder between the thumb and forefinger (both being quite dry) it may be made to fall as a shower of fine particles. These pass into the solution, and are seen to move slowly across the screen through the solution, dissolving as they go, in some cases disappearing, and often changing the concentration of the part of the solution through which they have passed, so as to produce obvious refraction effects. Finally, to show that the solution was supersaturated, add a few crystals of the hydrated salt, and crystallisation at once occurs. The anhydrous salt must be added as a shower of fine powder, as larger pieces may—by taking up water and forming crystals of the hydrated salt before they can dissolve—give rise to a general crystallisation of the solution.

(4). The peculiarity of the solubility in water of such substances as aniline, carbolic acid, &c., observed by Alexejew (*Wied. Ann.*, Bd. xxviii., 1886, p. 305), may readily be shown on the screen by using carbolic acid, whose critical temperature (the temperature above which it and water are mutually infinitely soluble) is about 69°C . For this purpose pour some of the acid into a long test-tube, about 12 or 15 m.m. diameter, and add water. The water will lie in a layer above the acid. Support the test-tube by a clip grasping it at the top, and focus on the screen. The line of demarcation between the two liquids will be evident. Now mix the liquids by stirring, and the whole becomes cloudy. Let the tube stand, and the liquid separates again into two layers, having different depths from those they had before, both being now solutions. As this process requires considerable time, the stirring may have been done beforehand. Next surround the test-tube by a beaker of boiling water, passing it upwards from below, and stir the liquids with a hot glass rod. A slight cloudiness appears, but the liquid quickly clears and is seen to have become homogeneous throughout, the line of demarcation having disappeared. If now the beaker of hot water be removed, and one of cold water be substituted for it, the liquid becomes cloudy, a strong solution separating out everywhere, and the little spherical masses of strong solution sinking and coalescing as they sink, to form larger spheres. After a time the liquid is seen to have again become separated into two layers. If the necessary time is not available, the separation into layers may be obtained very quickly by removing the beaker of cold water and again applying the hot bath, which, raising

the temperature, stops the separating out of the strong solution, and re-dissolves it in the surrounding weaker solution, thus producing a comparatively strong solution in the lower part of the tube and a comparatively weak one in the upper part. The experiment requires but a few minutes, and is both striking and instructive.

THE EFFECT ON BUTTER FROM FEEDING ON COTTON-SEED AND COTTON- SEED MEAL.*

By Prof. N. T. LUPTON, State Chemist.

An investigation was undertaken a few months ago at the Alabama Experiment Station to determine the effect of cotton-seed and cotton-seed meal on the composition of the butter fat, especially on the volatile acids, the melting-point, and the specific gravity of the butter produced.

Several chemists of late years have called attention to changes produced by the use of the feed stuffs mentioned, notably Prof. Harrington, of the Texas Experiment Station, and Dr. Wiley, of the Department of Agriculture, Washington, D.C. This subject was thought to be of sufficient scientific and practical importance to justify an extended investigation. For this purpose a herd of registered Jerseys was divided into two groups, one consisting of ten cattle and the other of a single cow. The cattle of the first group were fed for a preparatory period of ten days on the customary ration used at the station, excluding cotton-seed meal and hulls; the single cow was fed on the same ration. At the end of the preparatory period, samples of milk and butter were taken for one week, on Monday, Wednesday, and Friday, and carefully analysed. The milk of the ten cattle composing the first group was mixed and churned as a whole—that of the single cow was kept separate and churned by itself. The first preparatory period was for ten days; after that, the experimental and preparatory periods extended over seven days each.

The daily rations for the different periods, which repre-

* *Journal of the American Chemical Society*, Vol. xiii., No. 4.

sent the kind and quantity of food actually consumed, were as follows:—

First period, preparatory and experimental:—

Ground oats.. .. 5 lbs.
" corn 5 "
Bran 5 "

Nutritive ratio 1 : 5'8.

Second period:—

Cotton-seed meal . . . 3 lbs.
Ground oats.. .. 4 "
Bran 5 "
Ensilage 11 "

Nutritive ratio.. .. 1 : 3'75.

Third period:—

Cotton-seed meal . . . 4 lbs.
Cotton-seed hulls . . . 9 "
Ensilage 4½ "

Nutritive ratio.. .. 1 : 5'08.

During the fourth period the cattle were confined exclusively to raw cotton-seed and cotton-seed hulls, and during the fifth period to cooked cotton-seed and cotton-seed hulls. They were allowed as much as they would eat. The nutritive ratios mentioned above are calculated from analyses made of the feed stuffs in use at the station. In compounding the rations, the object was not so much to conform with strictness to the German standard as to bring the cows gradually under the influence of cotton-seed, cotton-seed meal, and hulls without injury to their general health.

The results of the analysis of samples of milk and butter, taken immediately after each milking and churning, are given below. The first two tables give the composition of each sample of milk analysed, also the volatile acids, melting-point, and specific gravity of the butter from the same milk; the third table gives the average composition for each experimental period.

The following table, taken from a record carefully kept at the dairy, gives the aggregate amount of milk and

Composition of Jersey milk for each day analysed.						Butter from same milk.			
Date.	Water.	Butter fat.	Cassin.	Sugar.	Ash.	Volatile acids. Expressed in c.c. one-tenth normal alkali for 5 grms. of fat.	Melting- point. C.	Specific gravity at 100° C.	Rations.
Group I.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.				
Nov. 19 ..	85'76	5'53	3'95	3'96	0'80	30'0	35'9°	0'90257	Period I. { 5 lbs. ground oats. " " corn. " " bran.
" 21 ..	84'95	5'20	4'05	5'09	0'81	29'6	35'3°	0'90311	
Dec. 1 ..	84'15	5'73	4'06	5'24	0'82	29'7	36'0°	0'90411	Period II. { 3 lbs. cotton-seed meal. 4 lbs. ground oats. " " bran. 11 lbs. ensilage.
" 3 ..	83'62	5'51	3'88	6'19	0'80	30'5	36'3°	0'90165	
" 5 ..	84'26	5'16	3'90	5'98	0'80	31'4	36'1°	0'90265	
Dec. 15 ..	84'53	5'96	3'64	5'12	0'75	28'4	36'6°	0'90081	Period III. { 4 lbs. cotton-seed meal. 9 lbs. cotton-seed hulls. 4½ lbs. ensilage.
" 17 ..	83'35	6'07	3'60	6'03	0'75	26'9	37'6°	0'90194	
" 19 ..	84'71	5'79	3'57	5'19	0'74	27'1	38'1°	0'90306	
Jan. 5 . ..	84'27	6'41	3'58	5'01	0'73	22'0	43'6°	0'90021	Period IV. { Raw cotton-seed. Cotton-seed hulls.
" 7 . ..	84'59	6'11	3'34	5'22	0'74	21'9	43'9°	0'89721	
" 9 . ..	84'51	5'84	3'56	5'37	0'72	22'4	43'4°	0'89955	
Jan. 19 ..	85'84	4'87	3'39	5'16	0'74	23'1	42'7°	0'90462	Period V. { Cooked cotton- seed. Cotton-seed hulls.
" 21 ..	84'89	5'95	3'31	5'08	0'77	22'2	42'3°	0'90057	
" 23 ..	85'38	5'53	3'31	5'04	0'74	22'1	43'0°	0'90266	

Composition of Jersey milk for each day analysed.						Butter from the same milk.			
Date.	Water.	Butter fat.	Casein.	Sugar.	Ash.	Volatiles acids.	Melting-point.	Specific gravity at 100° C.	Rations.
Group II.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Expressed in c.c. one-tenth normal alkali for 5 grms. of fat.	C.		
Nov. 24 ..	85.53	4.67	3.84	5.23	0.73	31.4	35.1°	0.90188	Period I. { 5 lbs. ground oats, 5 " " corn, 5 lbs. bran.
" 28 ..	84.03	5.93	3.93	5.30	0.81	31.5	33.4°	0.90458	
Dec. 8 ..	85.71	4.75	3.56	5.30	0.68	—	—	—	Period II. { 3 lbs. cotton-seed meal, 4 lbs. ground oats, 5 " bran, 11 lbs. ensilage.
" 10 ..	85.68	4.53	3.84	5.24	0.71	31.7	36.5°	0.90282	
" 12 ..	85.63	3.94	3.66	6.02	0.75	30.6	36.2°	0.90022	
Dec. 22 ..	85.26	4.74	3.42	5.86	0.72	25.5	37.5°	0.90192	Period III. { 4 lbs. cotton-seed meal, 9 lbs. cotton-seed hulls, 4½ lbs. ensilage.
Jan. 2 ..	84.31	5.85	3.69	5.42	0.73	25.4	41.3°	0.89798	
Jan. 12 ..	85.17	5.12	3.40	5.60	0.71	20.5	43.5°	0.89751	Period IV. { Raw cotton-seed. Cotton-seed hulls.
" 14 ..	85.10	4.76	3.47	5.98	0.69	19.2	41.0°	0.89929	
" 16 ..	85.54	4.80	3.34	5.64	0.68	21.4	43.0°	0.89883	
Jan. 26 ..	86.21	4.87	3.13	5.09	0.70	22.0	43.3°	0.89775	Period V. { Cooked cotton-seed. Cotton-seed hulls.
" 28 ..	86.00	4.88	3.12	5.28	0.72	22.1	43.3°	0.89994	
" 30 ..	85.39	6.00	3.18	4.72	0.71	21.7	44.0°	0.89803	

Average composition of Jersey milk during each period.						Butter from same milk.			
Period.	Water.	Butter fat.	Casein.	Sugar.	Ash.	Volatiles acids.	Melting-point.	Specific gravity at 100° C.	Rations.
Group I.									
I. ..	85.35	5.36	4.00	4.52	0.81	29.8	35.6°	0.90284	{ 5 lbs. each ground oats, ground corn, and bran.
II. ..	84.01	5.47	3.95	5.80	0.81	30.5	36.1°	0.90280	{ Cotton-seed meal, 3 lbs.; ground oats, 4 lbs.; bran, 5 lbs.; ensilage, 11 lbs.
III. ...	84.20	5.91	3.60	5.45	0.75	27.5	37.4°	0.90194	{ Cotton-seed meal, 4 lbs.; cotton-seed hulls, 9 lbs.; ensilage, 4½ lbs.
IV. ...	84.46	6.12	3.49	5.20	0.73	22.1	43.6°	0.89899	{ Raw cotton-seed meal and cotton-seed hulls.
V. ..	85.37	5.45	3.36	5.09	0.75	22.5	42.7°	0.90262	{ Cooked cotton-seed meal and cotton-seed hulls.
Group II.									
I. ..	84.78	5.30	3.89	5.26	0.77	31.4	34.2°	0.90323	{ 5 lbs. each ground oats, ground corn, and bran.
II. ..	85.67	4.41	3.69	5.52	0.71	31.1	36.3°	0.90152	{ Cotton-seed meal, 3 lbs.; ground oats, 4 lbs.; bran, 5 lbs.; ensilage.
III. ...	84.79	5.30	3.37	5.64	0.72	25.45	39.4°	0.89995	{ Cotton-seed meal, 4 lbs.; cotton-seed hulls, 9 lbs.; ensilage, 4½ lbs.
IV. ...	85.27	4.89	3.40	5.74	0.69	20.4	42.5°	0.89854	{ Raw cotton-seed meal and cotton-seed hulls.
V. ..	85.87	4.92	3.14	5.03	0.71	21.9	43.5°	0.89857	{ Raw cotton-seed and cotton-seed hulls.

butter produced by the first group, consisting of ten cows, for each experimental period of seven days:—

Period	Pounds of milk.	Pounds of butter.	Pounds of milk for one pound of butter.
I.	1414½	82	17'2+
" II.	1275	85½	14'9+
" III.	975	91	10'7+
" IV.	896	75	11'9
" V.	716	58	12'3+

As will be observed, there is a marked falling off in the quantity of milk, and a corresponding increase in the amount of butter produced during the first three periods, as the cattle were getting more under the influence of cotton-seed meal.

During the remaining periods the quantities of both milk and butter diminish, the ration being confined to cotton-seed and cotton-seed meal, without reference to having it well balanced as a milk ration.

The general effects of these valuable feed stuffs, when used in carefully prepared rations, will hereafter be investigated; at present we are concerned only, as previously stated, with their effects on the volatile acids, melting-point, and specific gravity of the butter fat produced under their influence. For these effects attention is called to the above tabular statements, from which the following conclusion is drawn:—

Feeding on cotton-seed and cotton-seed meal increases in a marked degree the melting-point of butter, the increase reaching in these experiments eight or nine degrees, and diminishes to a corresponding extent the volatile acids, while the specific gravity remains virtually the same.

The richness of cotton-seed meal in albumenoids renders it of prime importance to mix it with one or more feed stuffs poor in this nitrogenous compound, such as ensilage, hay, or cotton-seed hulls.

It may be stated in this connection that no change was observable in the colour of the butter from feeding cotton-seed and cotton-seed meal. The samples, still in the laboratory, are all of a beautiful golden yellow.

It is proper to state that the analytical work in the above tables was done by Dr. J. T. Anderson, first assistant in the chemical laboratory.

ELECTROLYTIC SEPARATIONS.

By EDGAR F. SMITH and FRANK MUHR.

HAVING found after many trials that gold could be completely precipitated by the current from solutions of potassio-auric cyanide, steps were taken to ascertain from what metals it could be separated. Former studies (*Amer. Chem. Jour.*, xii., 252) showed that a current of one-hundredth ampère did not precipitate palladium from a solution containing an excess of potassium cyanide until after it had acted for a period of thirty-six hours. This behaviour pointed to a possible separation of gold from palladium. These two metals were, therefore, experimented upon with the current, under the conditions indicated in the following table:—

	Gold present.	KCN.	Total dilution.	Current in c.c. OH gas per minute.	Palladium present.	Gold found.	Difference in percentage from theory.
	Grms.	Grms.	c.c.	C.c.	Grms.	Grms.	
1.	0'1162	1'50	150	0'80	0'1200	0'1162	—
2.	"	"	"	"	"	0'1163	+0'08
3.	"	"	"	"	"	0'1162	—
4.	"	"	"	"	"	0'1163	+0'08
5.	"	"	"	0'40	"	0'1160	—0'17
6.	"	"	"	"	"	0'1156	—0'52
7.	"	"	"	1'00	"	0'1164	+0'17
8.	"	"	"	"	"	0'1158	—0'34

The time allowed for the precipitation of the gold varied from twelve to fourteen hours. Cold and hot water were used for washing the precipitated metal. The deposits were made directly upon the platinum dishes. The gold was subsequently dissolved off by placing dilute potassium cyanide in the vessels, and then connecting the latter with the anode of a feeble Crowfoot battery (*Jour. Franklin Institute*, cxxxi., 300; *Jour. Anal. Chem.*, v., 205). The gold cyanide solution was decomposed with aqua regia, and, after obtaining gold chloride, this was carefully examined for palladium. None was discovered.

Gold from Copper.—The previous electrolytic separation of silver from copper (*Jour. Franklin Institute*, cxxix., 241) indicated that gold might perhaps be separated with equal facility from the latter metal, inasmuch as the complete deposition of the gold did not require a current much stronger than that necessary for the precipitation of silver. The separation proved successful under the conditions given below.

	Gold present.	KCN.	Total dilution.	Current in c.c. OH gas per minute.	Copper present.	Gold found.	Difference in percentage from theory.
	Grms.	Grms.	C.c.	C.c.	Grms.	Grms.	
9.	0'1725	1'5	150	0'8	0'1250	0'1725	—
10.	0'1725	3'5	"	0'4	"	0'1728	+0'17
11.	"	"	"	"	"	0'1720	—0'29
12.	"	"	"	"	"	0'1735	+0'30
13.	"	3	"	0'8	"	0'1736	+0'60

Copper was not detected in the precipitated gold. The time required for the precipitation, washing, and drying of the deposits was the same as in the separation of gold from palladium.

Gold from Cobalt.—In the electrolytic separation of mercury from cobalt, and of silver from cobalt (*Jour. Franklin Institute*, cxxix., 239, 244), satisfactory results were obtained only after the quantity of alkaline cyanide present had been reduced to 3 grms. This quantity was used in the following separations, although its increase was not accompanied by the difficulties attending the separation of the metals to which reference has just been made. Indeed, in this particular case no special effort was required in order to get satisfactory results.

	Gold present.	KCN.	Total dilution.	Current in c.c. OH gas per minute.	Cobalt present.	Gold found.	Difference in percentage from theory.
	Grms.	Grms.	C.c.	C.c.	Grms.	Grms.	
14.	0'1792	3	150	0'6	0'15—0'20	0'1789	—0'11
15.	"	"	"	"	"	0'1799	+0'49
16.	"	"	"	"	"	0'1794	+0'11
17.	"	"	"	"	"	0'1799	+0'49

The current acted upon the double cyanides through the night.

Gold from Nickel.—This separation can be made without difficulty, as is proved by the four trials given below.

	Gold present.	KCN.	Total dilution.	Current in c.c. OH gas per minute.	Nickel present.	Gold found.	Difference in percentage from theory.
	Grms.	Grms.	C.c.	C.c.	Grms.	Grms.	
18.	0'1725	2½	150	0'5	0'1373	0'1724	—0'05
19.	0'1725	3	"	1'0	"	0'1718	—0'49
20.	0'1467	2½	"	0'5	"	0'1462	—0'34
21.	"	"	"	"	"	0'1460	—0'48

The electrolytic separation of mercury from zinc in cyanide solution, as well as cadmium and silver from the latter metal, occurred without any special difficulty.

Gold from Zinc.—The current to decompose the double cyanide of zinc and potassium must yield at least 2–3 c.c. electrolytic gas per minute, so that special precautions in regard to the following separation need not be given:—

	Gold present.		Total dilution.	Current in c.c. OH gas per minute.	Zinc present.		Difference in percentage from theory.
	Grm.	KCN. Grms.			Grm.	Grm.	
22.	0.1792	3	150	0.5	0.2000	0.1796	+0.22
23.	"	"	"	0.6	"	0.1797	+0.27
24.	"	"	"	"	"	0.1790	-0.11
25.	"	"	"	"	"	0.1798	-0.33

It will be noticed in the preceding experiments that the gold is either slightly in excess or below the theoretical amount. This cannot be due to incomplete precipitation or to the co-precipitation of the other metal present in the double cyanide solution, for in each of the preceding cases careful search was made for all the metals operated upon; the variations from the theoretical requirements must therefore be attributed to some other cause. The precipitations were made in platinum dishes; these varied in weight from 60–71 grms. Care was not taken to weigh at any particular period of the day, nor were the precipitating vessels allowed any definite time for drying, &c.

The battery used to precipitate the gold consisted of 6–10 Crowfoot cells. The poles, during precipitation, were $1\frac{1}{2}$ inches apart. Cover-glasses were placed over the electrolysed solution to prevent loss and to exclude dust. The latter can easily cause the metal precipitated to collect in little spongy masses, which are readily detached upon washing. To determine when the gold was fully precipitated, the level of the liquid in the dish was raised by the addition of distilled water. Before the current was finally interrupted the poles were brought more closely together, and the electrolytic action continued for a half-hour longer. It is better to do this than to remove a portion of the liquid and apply some special test to it.

It is scarcely necessary to add that if the clean platinum surface remains uncoated, the precipitation of metal is finished.

The current of the strength given in the preceding experiments *does not precipitate* platinum either from hot or from cold solution of its double cyanide when an excess of alkali cyanide is present. In this respect platinum resembles palladium. This behaviour prompted us to attempt, with good results, the separations recorded in the following lines:—

Gold from Platinum.

	Gold present.		Total dilution.	Current in c.c. OH gas per minute.	Platinum pre- sent.		Difference in percentage from theory
	Grm.	KCN. Grms.			Grm.	Grm.	
26.	0.1467	2½	150 c.c.	1	0.2433	0.1474	+0.48
27.	"	"	"	"	"	0.1474	"
28.	"	"	"	"	"	0.1468	+0.05
29.	"	"	"	"	"	0.1461	-0.40

Silver from Platinum.—In the first trials of the separation of gold from platinum the dishes were coated with a thick layer of metallic silver. When the platinum double cyanide solution was electrolysed, platinum metal was deposited upon the silver. Its precipitation was,

however, incomplete; furthermore, silver passed into solution. This behaviour seemed to us to promise little in the way of separating silver from platinum. However, after dissolving definite amounts of salts of the two metals and adding an excess of potassium cyanide, the solution was directly electrolysed, when the silver separated upon the dish perfectly free from platinum. Currents of greater strength than that given in the recorded experiments will throw out traces of platinum. It shows itself in dark spots, distributed over the white silver surface. In such cases a black, though minute, residue will always be noticed when the precipitated silver is dissolved in dilute nitric acid. The results were as follows:—

	Silver present.		Total dilution.	Current in c.c. OH gas per minute.	Platinum pre- sent.		Difference in percentage from theory.
	Grm.	KCN. Grms.			Grm.	Grm.	
30.	0.0770	2½	150	1 c.c.	0.2433	0.0772	+0.25
31.	"	"	"	"	"	0.0768	-0.25

Cadmium from Platinum.—Reference to a paper by Smith and Frankel (*Amer. Chem. Journ.*, xii., 428) will disclose the fact that they failed to obtain an electrolytic separation of silver and cadmium from palladium. The separation of silver from platinum succeeds if conducted under the conditions outlined in the preceding example, but the separation of cadmium from platinum resulted negatively, although the current was reduced to 0.2 c.c. oxy-hydrogen gas per minute. The precipitated cadmium always contained platinum. We also found that if the platinum dishes were coated with cadmium and the double cyanide of platinum and potassium electrolysed in these vessels, the platinum metal was deposited quite rapidly; cadmium, however, invariably dissolved. This behaviour was similar to that observed in the attempted electrolytic separation of cadmium from palladium and from nickel.

Platinum, palladium, and nickel show many points of similarity in deportment when their double cyanide solutions are electrolysed.

Mercury from Platinum.—This separation is as readily made as that of mercury from palladium and nickel.

	Mercury pre- sent.		Total dilution.	Current in c.c. OH gas per minute.	Platinum pre- sent.		Difference in percentage from theory.
	Grm.	KCN. Grms.			Grm.	Grm.	
32.	0.1902	2½	150 c.c.	0.2	0.2433	0.1900	-0.10
33.	"	"	"	"	"	0.1904	+0.10
34.	"	"	"	"	"	0.1905	+0.15
35.	"	"	"	"	"	0.1910	+0.41

The separations of gold, silver, and mercury from platinum were carried out in the cold. The depositions were made in the same platinum vessels used in the experiments recorded in the first part of this communication. The deposited metals were treated as mentioned in previous papers. The time of precipitation occupied from fourteen to sixteen hours.—*American Chemical Journal*, xiii., No. 6.

The Illumination of the Scale in Polarising Apparatus.—H. Schneider. The author, instead of using a separate source of light, conducts the light of the flame which serves to illuminate the field of vision upon the scale by means of a reflecting glass rod, exactly on the principle upon which is founded the microscopic lamp of Kochs and Wolz.—*Zeitschrift*, xxix., Part 6.

SOME NOTES ON ELECTROLYTIC QUANTITATIVE SEPARATION OF METALS.

By T. O'CONNOR SLOANE, Ph.D.

It may seem somewhat presumptuous, after Classen's classic work in electrolytic analysis, to offer any suggestions as to the conducting of this class of quantitative determinations. But there is one point in the work which, it may safely be said, has been to a certain extent neglected. This point is the influence of electromotive force, or of difference of potential upon the separations.

In Classen's work upon the subject the voltage of the circuit is duly considered, and an elaborate rheostat for regulating the voltage within somewhat crude limits ($\frac{1}{2}$ volt) is described. This is in one of the introductory chapters. The rheostat is for use with a 600 watt dynamo. But the author also mentions batteries, and describes his method of conducting determinations with these sources of electromotive force. The current strength is then the standard, and it is determined by the volume of oxy-hydrogen gas which the current can liberate in a definite time. In other words, the amperage of the current alone receives direct attention. By using the same sized electrodes, the author states, the conditions are kept sensibly the same. Here we have an indirect recognition of the influence of electromotive force. But the attempted maintenance of the most uniform conditions is a poor reliance. The conditions will inevitably vary and the temperature of the room and gradual change of the nature of the solution operated on, will cause variations in resistance that will affect the difference of potential. To show how little regard is paid to voltage, we are directed in iron determinations to use two and sometimes three Bunsen cells. Any change in the number of cells in series would cause great variations in the voltage, in the case cited about 50 per cent. If the cells were kept in parallel and any resistance, such as that of a voltmeter, were in series with the decomposing apparatus, a great variation in voltage would even then ensue by changes in the number of cells.

The object of these notes is to plead for a greater recognition of the influence of difference of electric potential in analytical work. The facts of the case are these: For the decomposition of every solution a definite and absolutely fixed voltage is required. The strength of current affects only the condition of the deposit. Thus a current of any number of amperes might be passed through acidulated water without decomposing it until the voltage passed a fixed point, when decomposition would at once begin. A single gravity cell, large or small (sulphate of copper-zinc copper couple), cannot decompose water because its voltage is too low. The minutest bichromate cell will at once begin to decompose it, because its voltage is high enough.

Again, the amperage of the current should not be broadly stated without reference to absolutely fixed conditions of electrodes. The proper way would be to state it as referred to unit area of cathode and anode. Probably the cathode reference would be all that is needed. As ordinarily put the cathode is supposed to be a platinum dish of more or less definite size, filled with a variable depth of fluid, and the electrolytic gas set free in one or more minutes is given. All this tells nothing.

It would seem obvious that a definite and absolutely fixed difference of potential being required for the decomposition of each compound, the voltage could be made the basis for analytical work. It would be possible to effect successive separation of metals from the same solution by modifying the voltage, starting, of course, with the lowest. How far the precipitation of mixed metals, so called alloys, would interfere with such attempts is not definitely recorded. It amounts to nothing to state, as is done, that a weaker current than is required for iron or some other metals will precipitate copper. The strength of the current has nothing to do

with it. It is the difference of potential that affects the result. The varying of such difference corresponding in a general way with the strength of the current, as the operations were conducted, has doubtless occasioned the confusion.

In stating the results of, or giving directions for conducting electrolytic separations, two factors should always be stated. One is the difference of potential, the other the amperage per unit area of cathode. Then something definite would be known. It seems probably that by working on these lines some exceedingly interesting results in the way of double decompositions, as well as of separations, might be obtained.

Should any such result be obtained as the determining of a series of potential differences available for separations of metals from single solutions it would be highly interesting. The heat of combination of a vast number of compounds has been obtained and is readily reduced to volts, but such reduction is theoretical and does not accurately hold for all cases. The principal trouble would lie in the regulation of the voltage. But at the least there seems ground for research in the direction here suggested.—*Journal of the American Chemical Society*, xiii., No. 4.

FOREIGN TRADE AND METRIC WEIGHTS AND MEASURES.

FROM the Consular Report (No. 922) presented to Parliament in July, 1891, on the trade and finance of Japan, it appears that hitherto the railway plant has been mostly of English make. The locomotives, however, are chiefly made in America or Germany, and it is stated that the superior finish of French and other Continental material is now a great recommendation in the eyes of the Japanese government departments. Last, but not least, the fact that the metric scale is in use in Japan also leads to a preference being given to Continental material.

We also learn that the Russian government has at last decided to make the adoption of the metric weights and measures compulsory in medical and pharmaceutical work, and it is intended that this system shall be gradually extended to all other branches of science.

There is, no doubt, a growing tendency to adopt the metric weights and measures throughout the civilised world, and it is becoming more and more important that, as a measure of self defence, if for no other reason, we should adopt them in England. In these days of keen competition with Belgian, French, German, and other foreign makers, we cannot afford to let them have the advantage of offering machines and other articles made according to the metric scale as required by so many foreign buyers, whilst we perplex them with our troublesome, unsystematised, and absurd weights and measures.

NOTICES OF BOOKS.

The Foundations of Chemistry. (Grundlagen der Chemie). Parts 3, 4, and 5. By D. MENDELEEFF, Professor at the University of St. Petersburg. Translated from the Russian by L. JAWIN and A. THILLOT. St. Petersburg: Carl Ricker.

In these three parts the author expounds the laws of Gay-Lussac and Avogadro, the doctrine of Berthelot, the principles of spectroscopic research, and the periodic law.

When speaking of the revelations of the spectroscope he repeats the statement that "in the universe the elementary bodies are everywhere the same as on our earth, and that—even at the high temperature which prevails in the sun—there occurs no destruction or modification of those bodies which we regard as the elements of che-

mistry." Here, again, he overlooks the increasing complexity of the spectra of the self-luminous heavenly bodies as their temperature diminishes. Moreover, those who question the absolute simplicity of our conventional elements do not assert that certain such bodies are destroyed by the heat of the sun, but that they are formed only when or where such heat has declined.

Prof. Mendeleeff further remarks that "the astronomer may easily fall into errors if he draws conclusions as to the composition of simple bodies from the spectra of the stars." He admits the existence of helium as possible, but he combats the views of Lockyer on the spectrum of iron as observed in the solar atmosphere. He alleges that "the concepts of the simple body and the element are in every respect better established than any results of spectroscopic investigations, that the relatively novel theory of the spectra of simple bodies is merely a result of the chemical theory of simple bodies, and that, as regards the spectroscopic phenomena, with the exception of Kirchhoff's law, no generalisations are possible which would allow us to foresee phenomena, whilst the theory of simple bodies has already reached that state." This reasoning will scarcely be accepted as conclusive by minds free from preconceptions.

The Periodic Law is naturally discussed at some length. The author states, doubtless truthfully, that the works of De Chancourtois (*vis tellurique*) and Newlands were unknown to him when he first published his researches on this subject. It seems, however, that scant justice is done to Mr. Newlands in the words that in his memoirs "some germs of the periodic law may be seen," and in placing him merely on a level with De Chancourtois whose very meaning seems to have escaped recognition in France, as well as abroad, until the appearance of M. de Boisbaudran's memoir at the beginning of the present year.

If we rightly understand the somewhat ambiguous language of Prof. Mendeleeff, he denies that Prof. Lothar Meyer had any original share in the recognition of the periodic law. The Russian *savant* considers it evident that Meyer "accepted the periodic law in the form in which I presented it."

Leaving such inquiries, we may venture to pronounce it strange that the author should so earnestly seek to uphold the simple and primordial character of the elements when his own labours have done so much to prove their genetic connection. It is, however, by no means unexampled for the discoverer of a fact or a truth to object to its results.

Prof. Mendeleeff points out that "the laws of Nature tolerate no exceptions, and differ thus from the rules, e.g., of grammar." Hence spring at once the educational value of Science, and the cause of the ill-will with which it is regarded by the "humanists."

CORRESPONDENCE.

ON THE DETERMINATION OF THE AMOUNT OF FATTY MATTER PRESENT IN OLEINE (TURKEY RED OIL).

To the Editor of the Chemical News.

SIR,—Owing to absence from home I have not had an opportunity of replying to Mr. Wilson's letter (CHEMICAL NEWS, vol. lxiv., p. 49) until now. The three samples of oleine, containing definite proportions of fatty matter, referred to in my paper (CHEM. NEWS, vol. lxiv., p. 15), were made in the following manner:—First of all, the sulpho-fatty acids were prepared in the usual way from three different specimens of castor oil, and purified as thoroughly as possible by long standing in a separating-funnel, running off the bottom layer occasionally, until

no further separation took place. The sulpho-fatty acids were then left over vitriol in a desiccator for about a week. By operating in this manner the fatty matters are obtained in a practically dry state. Oleine containing any required percentage of fatty matter may then be easily prepared, all the ingredients being of course carefully weighed.

Mr. Wilson complains that I "charge him with the grave error of not comparing the ether extraction method with some standard process," but I think he has slightly misunderstood me. The meaning which I certainly intended to convey was, that it would have been better if he had tested the accuracy of his method, not against a standard process, but upon what may be termed a "standard sample" of oleine, viz., one containing a known percentage of fatty matter.—I am, &c.,

ROWLAND WILLIAMS.

Laboratory and Assay Office,
28, Pall Mall, Manchester, Aug. 8, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 4, July 27, 1891.

Examination of Samples of Native Iron of Terrestrial Origin discovered in the Gold-Washings near Berezowak.—M. Daubrée and Stanislas Meunier.—The metal is very magnetic, but manifests no polarity. Its specific gravity, determined on a specimen weighing 33.821 grms. is at 17°=7.59. A surface cut and polished is brilliant and of the ordinary colour of iron. If treated with an acid it is attacked uniformly without giving the well-known Widmannstett figures characteristic of meteoric iron. This fact, taken along with the absence of nickel, leads to the inference that this iron is not of extra terrestrial origin. Small quantities of platinum are present, probably from a mixture of ferriferous platinum with the native iron.

The Volatility of Nickel on Treatment with Hydrochloric Acid.—A. Schützenberger.—If anhydrous nickel chloride is reduced at a dull red heat with dry hydrogen gas, it is found that the hydrochloric gas escaping from the reduction-tube carries along with it sensible quantities of metal in the form of a volatile product. Special arrangements showed that this is not a case of simple mechanical transportation. The author suggests three hypotheses; the product may be a nickel hydride, which is scarcely probable, or there is formed a nickel hydrochlorate or a hydrochlorate of the chloride $\text{NiCl}_2 \cdot x(\text{ClH})$. Iron and zinc are transported in a similar manner.

The Densities of Oxygen, Hydrogen, and Nitrogen.—A. Leduc.—The densities of the three gases are within less than 1-10,000th part—

Hydrogen	0.0695
Oxygen	1.1050
Nitrogen	0.9720

From these values the mean centesimal proportion may be deduced as 23.235 by weight and 21.026 by volume. According to these experiments the atomic weight of nitrogen would be 13.99, and that of oxygen 15.905.

Remarks on the Transportation of Metallic Iron and Nickel by Carbon Monoxide.—Jules Garnier.—The author gives an instance of the transfer of iron observed in blast furnaces at Vierzon. Another case occurred in refining ferro-nickel on the sole of a Siemens-Martin furnace at Septèmes, where dust of metallic nickel was collected in flues which served to convey the escaping gases to a draught chimney at a considerable distance

from the furnaces. In a third case, a mixture of metallic nickel, steel, and cast iron, containing about 20 per cent of nickel, covered with a layer of flux, had been melted in a graphite crucible. When the crucible was removed from the furnace and the cover removed, there rose up a sheaf of sparks to the height of 6 metres; two-thirds of the metal were thus lost.

Action of Water upon Basic Salts of Copper.—G. Rousseau and G. Tite.—Water converts a great number of neutral metallic salts into basic salts by a process the laws of which have been discovered by M. Ditté. Some of these basic salts are brought to the state of oxides, as it occurs with antimony oxychloride and certain borates. The authors examine if the prolonged action of water at a sufficiently high temperature does not produce an analogous decomposition of other basic salts.

A Mode of the Present Formation of Mineral Sulphides.—E. Chuard.—The author, after referring to the observations of Daubrée (*Comptes Rendus*, vol. lxxx., p. 461), on the formation of mineral species in hot sulphur springs points out that mineral sulphides occur to such an extent in the superficial strata of the globe that we cannot ascribe their formation to this cause alone.

Researches on Thallium.—C. Lepierre and Lachaud.—The authors have studied the action of dilute potassa upon thallium chromate, that of concentrated potassa, that of melting potassa upon thallous chromate, that of melted potassium nitrate upon the same chromate, and lastly, they have examined thallium chloro-chromate.

On the Parabanic and Oxaluric Acids.—W. C. Matignon.—The author investigates these acids from a thermo-chemical point of view.

Transformation of Gallic Acid and of Tannic into Benzoic Acid.—Ch. Er. Guignet.—A mixture of ammonia and zinc powder is placed in a flask closed with a stopper, through which passes a tube drawn out to a point. Heat is applied, and when the evolution of hydrogen is quite regular a hot solution of gallic acid is gradually added. If the temperature is kept at 60°, the gallic acid is completely transformed in a few hours. It is changed first into salicylic and then into benzoic acid. Under the same conditions tannin (digallic acid) is also converted into benzoic acid.

Acid Polymers of Ricinoleic Acid.—M. Scheurer-Kestner.—Polymerisation may be pushed as far as to the tetra- and pentaricinoleic acids. As the polymerisation advances, the acid properties of the new compounds decrease.

On Panary Fermentation.—Léon Boutroux.—Panary fermentation consists essentially in the normal alcoholic fermentation of the sugar pre-existing in the flour. The leaven produces the disengagement of gases which raise the bread, and it hinders the development of the parasitic bacteria of the flour and the water from turning the paste sour and dissolving the gluten.

Transformation of Oxycarbonated Hæmoglobine and Methæmoglobine, and on a New Method of Detecting Carbon Monoxide in Blood.—H. Bertin-Sans and J. Moitessier.—These researches contradict the conclusions of Th. Weil and B. von Anrep regarding the existence of a combination of methæmoglobine with carbon monoxide. The carbonic oxide contained in the solutions of methæmoglobine behaves exactly as if it was dissolved in water. Hence it is easy to detect minimum quantities of carbon monoxide in blood.

Zeitschrift für Analytische Chemie.
Vol. xxix., Part 6.

Determination of Sugars with Copper-Potassium Carbonate.—H. Ost.—This memoir is too long for insertion in full, and does not admit of useful abstraction.

Orsat's Apparatus for the Analysis of Chimney Gases.—(See page 74).

The Determination of Nitric and Nitrous Acids in Spring Waters.—Max Rosenfeld.—This paper will be inserted in full.

Determination of the Ignition Temperature of Explosives.—Ch. E. Monroe.—From the *Four. Amer. Chem. Soc.*

Apparatus for Determining Carbonic Acid in Carbonates.—M. Finkener.—This paper requires the accompanying figure.

Determination of Dry Matter in Fibrous Material.—O. Knöfler (*Papier Zeitung*).—Already inserted.

Small Laboratory Appliances: Filtration with Reduced Pressure.—J. F. Stoddart.—From the *Four. Anal. Chem.*

Treatment of Filter Paper with Nitric Acid at 142°.—This device is successful, as the paper is not only strengthened but filters better.

A Vacuum Apparatus for Small Laboratories.—E. Dietrich (*Pharm. Central Halle*).—The air is rarefied by means of a water-pump.

Notes on Sodium Carbonate.—R. Kissling and L. Dobbin.—For the substance of this note we must refer to the *Zeit. für Angew. Chemie*.

New Determinations of the Specific Gravity of Sulphuric Acid of Different Strengths.—G. Lunge and Isler.—A series of tables.

On Lacmoid.—O. Foerster.—This paper will be inserted in full.

The Behaviour of Acids with Litmus.—J. E. Marsh.—From the *CHEMICAL NEWS*.

On Electrolysis.—Edgar F. Smith and Lee K. Frankel.—From the *Amer. Chem. Four.*, the *Four. Anal. Chem.*, and the *Four. Franklin Institute*.

A Volumetric Method for Determining Sulphuric Acid in Sulphates.—Launcelot W. Andrews.—From the *Amer. Chem. Four.*

The Reduction of Barium Sulphate to Sulphide on Ignition with the Carbon of the Filter.—C. W. Marsh (*Four. Anal. Chem.*).

Determination of Silica in Silicates by Fusion with Alkaline Silicates.—James P. Gilbert.—From the *Tech. Quart.*, with reference to papers on the same subject by George Craig and David Lindo (*CHEMICAL NEWS*).

A Modification of Elementary Analysis with Lead Chromate.—Rudolf de Roode.—From the *Amer. Chem. Four.*

The Simultaneous Determination of Sulphur and Carbon.—L. Prunier.—From the *Comptes Rendus*.

Determination of Sulphur in Organic Substances.—W. Burton.—From the *Amer. Chem. Four.*

Determination of Acetone in Wood Spirit.—L. Vignon and G. Arachequesne.—From the *Comptes Rendus*.

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BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

CARDIFF, 1891.

ADDRESS OF THE PRESIDENT,

WILLIAM HUGGINS, ESQ.,
D.C.L. (Oxon.), LL.D. (Cantab., Edin., et Dubl.),
Ph.D. (Lugd. Bat.), F.R.S., F.R.A.S., Hon. F.R.S.E., &c.,
Correspondant de l'Institut de France.

It is now many years since this Association has done honour to the science of Astronomy in the selection of its President.

Since Sir George Airy occupied the Chair in 1851, and the late Lord Wrottesley nine years later in 1860, other sciences have been represented by the distinguished men who have presided over your meetings.

The very remarkable discoveries in our knowledge of the heavens which have taken place during this period of thirty years—one of amazing and ever-increasing activity in all branches of science—have not passed unnoticed in the addresses of your successive Presidents; still it seems to me fitting that I should speak to you to-night chiefly of those newer methods of astronomical research which have led to those discoveries, and which have become possible by the introduction since 1860 into the observatory of the spectroscope and the modern photographic plate.

In 1866 I had the honour of bringing before this Association, at one of the evening lectures, an account of the first-fruits of the novel and unexpected advances in our knowledge of the celestial bodies which followed rapidly upon Kirchhoff's original work on the solar spectrum and the interpretation of its lines.

Since that time a great harvest has been gathered in the same field by many reapers. Spectroscopic astronomy has become a distinct and acknowledged branch of the science, possessing a large literature of its own and observatories specially devoted to it. The more recent discovery of the gelatine dry plate has given a further great impetus to this modern side of astronomy, and has opened a pathway into the unknown of which even an enthusiast thirty years ago would scarcely have dared to dream.

In no science, perhaps, does the sober statement of the results which have been achieved appeal so strongly to the imagination, and make so evident the almost boundless powers of the mind of man. By means of its light alone to analyse the chemical nature of a far distant body; to be able to reason about its present state in relation to the past and future; to measure within an English mile or less per second the otherwise invisible motion which it may have towards or from us; to do more, to make even that which is darkness to our eyes light, and from vibrations which our organs of sight are powerless to perceive to evolve a revelation in which we see mirrored some of the stages through which the stars may pass in their slow evolutionary progress—surely the record of such achievements, however poor the form of words in which they may be described, is worthy to be regarded as the scientific epic of the present century.

I do not purpose to attempt a survey of the progress of spectroscopic astronomy from its birth at Heidelberg in 1859, but to point out what we do know at present, as distinguished from what we do not know, of a few only

of its more important problems, giving a prominent place, in accordance with the traditions of this chair, to the work of the last year or two.

In the spectroscope itself advances have been made by Lord Rayleigh by his discussion of the theory of the instrument, and by Professor Rowland in the construction of concave gratings.

Lord Rayleigh has shown that there is not the necessary connection, sometimes supposed, between dispersion and resolving power, as besides the prism or grating other details of construction and of adjustment of a spectroscope must be taken into account.

The resolving power of the prismatic spectroscope is proportional to the length of path in the dispersive medium. For the heavy flint glass used in Lord Rayleigh's experiments the thickness necessary to resolve the sodium lines came out 1.02 c.m. If this be taken as a unit the resolving power of a prism of similar glass will be in the neighbourhood of the sodium lines equal to the number of c.m. of its thickness. In other parts of the spectrum the resolving power will vary inversely as the third power of the wave-length, so that it will be eight times as great in the violet as in the red. The resolving power of a spectroscope is therefore proportional to the total thickness of the dispersive material in use, irrespective of the number, the angles, or the setting of the separate prisms into which, for the sake of convenience, it may be distributed.

The resolving power of a grating depends upon the total number of lines on its surface and the order of spectrum in use, about 1000 lines being necessary to resolve the sodium lines in the first spectrum.

As it is often of importance in the record of observations to state the efficiency of the spectroscope with which they were made, Professor Schuster has proposed the use of a unit of purity as well as of resolving power, for the full resolving power of a spectroscope is realised in practice only when a sufficiently narrow slit is used. The unit of purity also is to stand for the separation of two lines differing by one-thousandth of their own wave-length; about the separation of the sodium pair at D.

A further limitation may come in from the physiological fact that, as Lord Rayleigh has pointed out, the eye when its full aperture is used is not a perfect instrument. If we wish to realise the full resolving power of a spectroscope, therefore, the emergent beam must not be larger than about one-third of the opening of the pupil.

Up to the present time the standard of reference for nearly all spectroscopic work continues to be Ångström's map of the solar spectrum, and his scale based upon his original determinations of absolute wave-length. It is well known, as was pointed out by Thalén in his work on the spectrum of iron in 1884, that Ångström's figures are slightly too small in consequence of an error existing in a standard metre used by him. The corrections for this have been introduced into the tables of the wave-lengths of terrestrial spectra collected and revised by a Committee of this Association from 1885 to 1887. Last year the Committee added a table of corrections to Rowland's scale.

The inconvenience caused by a change of standard scale is, for a time at least, considerable; but there is little doubt that in the near future Rowland's photographic map of the solar spectrum, and his scale based on the determinations of absolute wave-length by Pierce and Bell, or the Potsdam scale based on original determinations by Müller and Kempf, which differs very slightly from it, will come to be exclusively adopted.

The great accuracy of Rowland's photographic map is due chiefly to the introduction by him of concave gratings, and of a method for their use, by which the problem of the determination of relative wave-lengths is simplified to measures of coincidences of the lines in different spectra by a micrometer.

The concave grating and its peculiar mounting, in which no lenses or telescope are needed, and in which all

the spectra are in focus together, formed a new departure of great importance in the measurement of spectral lines. The valuable method of photographic sensitizers for different parts of the spectrum has enabled Professor Rowland to include in his map the whole visible solar spectrum, as well as the ultra-violet portion as far as it can get through our atmosphere. Some recent photographs of the solar spectrum, which include A, by Mr. George Higgs, are of great technical beauty.

During the past year the results of three independent researches have appeared, in which the special object of the observers has been to distinguish the lines which are due to our atmosphere from those which are truly solar—the maps of M. Thollon, which, owing to his lamented death just before their final completion, have assumed the character of a memorial of him; maps by Dr. Becker; and sets of photographs of a high and a low sun by Mr. McClean.

At the meeting of this Association in Bath, M. Janssen gave an account of his own researches on the terrestrial lines of the solar spectrum, which owe their origin to the oxygen of our atmosphere. He discovered the remarkable fact that while one class of bands varies as the density of the gas, other diffuse bands vary as the square of the density. These observations are in accordance with the work of Egoroff and of Olszewski, and of Liveing and Dewar on condensed oxygen. In some recent experiments Olszewski, with a layer of liquid oxygen 30 m.m. thick, saw, as well as four other bands, the band coincident with Fraunhofer's A—a remarkable instance of the persistence of absorption through a great range of temperature. The light which passed through the liquid oxygen had a light blue colour resembling that of the sky.

Of not less interest are the experiments of Knut Ångström, which show that the carbonic acid and aqueous vapour of the atmosphere reveal their presence by dark bands in the invisible infra-red region, at the positions of bands of emission of these substances.

It is now some thirty years since the spectroscope gave us for the first time certain knowledge of the nature of the heavenly bodies, and revealed the fundamental fact that terrestrial matter is not peculiar to the solar system, but is common to all the stars which are visible to us.

In the case of a star such as Capella, which has a spectrum almost identical with that of the sun, we feel justified in concluding that the matter of which it is built up is similar, and that its temperature is also high, and not very different from the solar temperature. The task of analysing the stars and nebulae becomes, however, one of very great difficulty when we have to do with spectra differing from the solar type. We are thrown back upon the laboratory for the information necessary to enable us to interpret the indications of the spectroscope as to the chemical nature, the density and pressure, and the temperature of the celestial masses.

What the spectroscope immediately reveals to us are the waves which were set up in the ether filling all interstellar space, years or hundreds of years ago, by the motions of the molecules of the celestial substances. As a rule it is only when a body is gaseous and sufficiently hot that the motions within its molecules can produce bright lines and a corresponding absorption. The spectra of the heavenly bodies are, indeed, to a great extent absorption spectra, but we have usually to study them through the corresponding emission spectra of bodies brought into the gaseous form and rendered luminous by means of flames or of electric discharges. In both cases, unfortunately, as has been shown recently by Professors Liveing and Dewar, Wüllner, E. Wiedemann, and others, there appears to be no certain direct relation between the luminous radiation as shown in the spectroscope and the temperature of the flame, or of the gaseous contents of the vacuum tube—that is, in the usual sense of the term as applied to the mean motion of all the molecules. In both cases the vibratory motions within the molecules to

which their luminosity is due are almost always much greater than would be produced by encounters of molecules having motions of translation no greater than the average motions which characterise the temperature of the gases as a whole. The temperature of a vacuum tube through which an electric discharge is taking place may be low, as shown by a thermometer, quite apart from the consideration of the extreme smallness of the mass of gas; but the vibrations of the luminous molecules must be violent in whatever way we suppose them to be set up by the discharge. If we take Schuster's view, that comparatively few molecules are carrying the discharge, and that it is to the fierce encounters of these alone that the luminosity is due, then if all the molecules had similar motions the temperature of the gas would be very high.

So in flames where chemical changes are in progress, the vibratory motions of the molecules which are luminous may be, in connection with the energy set free in these changes, very different from those corresponding to the mean temperature of the flame.

Under the ordinary conditions of terrestrial experiments, therefore, the temperature or the mean vis viva of the molecules may have no direct relation to the total radiation, which, on the other hand, is the sum of the radiation due to each luminous molecule.

These phenomena have recently been discussed by Ebert from the standpoint of the electro-magnetic theory of light.

Very great caution is therefore called for when we attempt to reason by the aid of laboratory experiments to the temperature of the heavenly bodies from their radiation, especially on the reasonable assumption that in them the luminosity is not ordinarily associated with chemical changes or with electrical discharges, but is due to a simple glowing from the ultimate conversion into molecular motion of the gravitational energy of shrinkage.

In a recent paper Stas maintains that electric spectra are to be regarded as distinct from flame spectra and from researches of his own; that the pairs of lines of the sodium spectrum other than D are produced only by disruptive electric discharges. As these pairs of lines are found reversed in the solar spectrum, he concludes that the sun's radiation is due mainly to electric discharges. But Wolf and Diacon, and later, Watts, observed the other pairs of lines of the sodium spectrum when the vapour was raised above the ordinary temperature of the Bunsen flame. Recently Liveing and Dewar saw easily, besides D, the citron and green pairs, and sometimes the blue pair and the orange pair, when hydrogen charged with sodium vapour was burning at different pressures in oxygen. In the case of sodium vapour, therefore, and presumably in all other vapours and gases, it is a matter of indifference whether the necessary vibratory motion of the molecules is produced by electric discharges or by flames. The presence of lines in the solar spectrum which we can only produce electrically is an indication, however, as Stas points out, of the high temperature of the sun.

We must not forget that the light from the heavenly bodies may consist of the combined radiations of different layers of gas at different temperatures, and possibly be further complicated to an unknown extent by the absorption of cooler portions of gas outside.

Not less caution is needed if we endeavour to argue from the broadening of lines and the coming in of a continuous spectrum as to the relative pressure of the gas in the celestial atmospheres. On the one hand it cannot be gainsaid that in the laboratory the widening of the lines in a Plücker's tube follows upon increasing the density of the residue of hydrogen in the tube, when the vibrations are more frequently disturbed by fresh encounters, and that a broadening of the sodium lines in a flame at ordinary pressure is produced by an increase of the quantity of sodium in the flame; but it is doubtful if pressure, as distinguished from quantity, does produce an increase of the breadth of the lines. An individual molecule of sodium will be sensibly in the same condition,

considering the relatively enormous number of the molecules of the other gases, whether the flame is scantily or copiously fed with the sodium salt. With a small quantity of sodium vapour the intensity will be feeble, except near the maximum of the lines; when, however, the quantity is increased, the comparative transparency on the sides of the maximum will allow the light from the additional molecules met with in the path of the visual ray to strengthen the radiation of the molecules farther back, and so increase the breadth of the lines.

In a gaseous mixture it is found, as a rule, that at the same pressure or temperature, as the encounters with similar molecules become fewer, the spectral lines will be affected as if the body were observed under conditions of reduced quantity or temperature.

In their recent investigation of the spectroscopic behaviour of flames under various pressures up to forty atmospheres, Professors Liveing and Dewar have come to the conclusion that though the prominent feature of the light emitted by flames at high pressure appears to be a strong continuous spectrum, there is not the slightest indication that this continuous spectrum is produced by the broadening of the lines of the same gases at low pressure. On the contrary, photometric observations of the brightness of the continuous spectrum, as the pressure is varied, show that it is mainly produced by the mutual action of the molecules of a gas. Experiments on the sodium spectrum were carried up to a pressure of forty atmospheres without producing any definite effect on the width of the lines which could be ascribed to the pressure. In a similar way the lines of the spectrum of water showed no signs of expansion up to twelve atmospheres; though more intense than at ordinary pressure, they remained narrow and clearly defined.

It follows, therefore, that a continuous spectrum cannot be considered, when taken alone, as a sure indication of matter in the liquid or the solid state. Not only, as in the experiments already mentioned, such a spectrum may be due to gas when under pressure, but, as Maxwell pointed out, if the thickness of a medium, such as sodium vapour, which radiates and absorbs different kinds of light, be very great, and the temperature high, the light emitted will be of exactly the same composition as that emitted by lamp-black at the same temperature, for the radiations which are feebly emitted will be also feebly absorbed, and can reach the surface from immense depths. Schuster has shown that oxygen, even in a partially exhausted tube, can give a continuous spectrum when excited by a feeble electric discharge.

Compound bodies are usually distinguished by a banded spectrum; but on the other hand such a spectrum does not necessarily show the presence of compounds, that is, of molecules containing different kinds of atoms, but simply of a more complex molecule, which may be made up of similar atoms, and be therefore an allotropic condition of the same body. In some cases, for example, in the diffuse bands of the absorption spectrum of oxygen, the bands may have an intensity proportional to the square of the density of the gas, and may be due either to the formation of more complex molecules of the gas with increase of pressure, or it may be to the constraint to which the molecules are subject during their encounters with one another.

It may be thought that at least in the coincidences of bright lines we are on the solid ground of certainty, since the length of the waves set up in the ether by a molecule, say of hydrogen, is the most fixed and absolutely permanent quantity in nature, and is so of physical necessity, for with any alteration the molecule would cease to be hydrogen.

Such would be the case if the coincidence were certain; but an absolute coincidence can be only a matter of greater or less probability, depending on the resolving power employed, on the number of the lines which correspond, and on their characters. When the coincidences are very numerous, as in the case of iron and the solar

spectrum, or the lines are characteristically grouped, as in the case of hydrogen and the solar spectrum, we may regard the coincidence as certain; but the progress of science has been greatly retarded by resting important conclusions upon the apparent coincidence of single lines, in spectroscopes of very small resolving power. In such cases, unless other reasons supporting the coincidence are present, the probability of a real coincidence is almost too small to be of any importance, especially in the case of a heavenly body which may have a motion of approach or of recession of unknown amount.

But even here we are met by the confusion introduced by multiple spectra, corresponding to different molecular groupings of the same substance; and, further, to the influence of substances in vapour upon each other; for when several gases are present together, the phenomena of radiation and reversal by absorption are by no means the same as if the gases were free from each other's influence, and especially is this the case when they are illuminated by an electric discharge.

I have said as much as time will permit, and I think indeed sufficient, to show that it is only by the laborious and slow process of most cautious observation that the foundations of the science of celestial physics can be surely laid. We are at present in a time of transition when the earlier, and, in the nature of things, less precise observations are giving place to work of an order of accuracy much greater than was formerly considered attainable with objects of such small brightness as the stars.

The accuracy of the earlier determinations of the spectra of the terrestrial elements are in most cases insufficient for modern work on the stars as well as on the sun. They fall much below the scale adopted in Rowland's map of the sun, as well as below the degree of accuracy attained at Potsdam by photography in a part of the spectrum for the brighter stars. Increase of resolving power very frequently breaks up into groups, in the spectra of the sun and stars, the lines which had been regarded as single, and their supposed coincidences with terrestrial lines fall to the ground. For this reason many of the early conclusions, based on observation as good as it was possible to make at the time with the less powerful spectroscopes then in use, may not be found to be maintained under the much greater resolving power of modern instruments.

The spectroscope has failed as yet to interpret for us the remarkable spectrum of the Aurora Borealis. Undoubtedly in this phenomenon portions of our atmosphere are lighted up by electric discharges; we should expect, therefore, to recognise the spectra of the gases known to be present in it. As yet we have not been able to obtain similar spectra from these gases artificially, and especially we do not know the origin of the principal line in the green, which often appears alone, and may have therefore an origin independent of that of the other lines. Recently the suggestion has been made that the Aurora is a phenomenon produced by the dust of meteors and falling stars, and that near positions of certain auroral lines to lines or flutings of manganese, lead, barium, thallium, iron, &c., are sufficient to justify us in regarding meteoric dust in the atmosphere as the origin of the auroral spectrum. Liveing and Dewar have made a conclusive research on this point, by availing themselves of the dust of excessive minuteness thrown off from the surface of electrodes of various metals and meteorites by a disruptive discharge, and carried forward into the tube of observation by a more or less rapid current of air or other gas. These experiments prove that metallic dust, however fine, suspended in a gas will not act like gaseous matter in becoming luminous with its characteristic spectrum in an electric discharge, similar to that of the Aurora. Professor Schuster has suggested that the principal line may be due to some very light gas which is present in too small a proportion to be detected by chemical analysis, or even by the spectroscope in the

presence of the other gases near the earth, but which, at the height of the auroral discharges, is in a sufficiently greater relative proportion to give a spectrum. Lemström, indeed, states that he saw this line in the silent discharge of a Holtz machine on a mountain in Lapland. The lines may not have been obtained in our laboratories from the atmospheric gases, on account of the difficulty of reproducing in tubes with sufficient nearness the conditions under which the auroral discharges take place.

In the spectra of comets the spectroscopic has shown the presence of carbon presumably in combination with hydrogen, and also sometimes with nitrogen; and in the case of comets approaching very near the sun, the lines of sodium, and other lines which have been supposed to belong to iron. Though the researches of Professor H. A. Newton and of Professor Schiaparelli leave no doubt of the close connection of comets with corresponding periodic meteor swarms, and therefore of the probable identity of cometary matter with that of meteorites, with which the spectroscopic evidence agrees, it would be perhaps unwise at present to attempt to define too precisely the exact condition of the matter which forms the nucleus of the comet. In any case the part of the light of the comet, which is not reflected solar light, can scarcely be attributed to a high temperature produced by the clashing of separate meteoric stones set up within the nucleus by the sun's disturbing force. We must look rather to disruptive electric discharges produced probably by processes of evaporation due to increased solar heat, which would be amply sufficient to set free portions of the occluded gases into the vacuum of space. May it be that these discharges are assisted, and indeed possibly increased, by the recently discovered action of the ultra-violet part of the sun's light? Lenard and Wolf have shown that ultra-violet light can produce a discharge from a negatively electrified piece of metal, while Hallwachs and Righi have shown further that ultra-violet light can even charge positively an unelectrified piece of metal. Similar actions on cometary matter, unscreened as it is by an absorptive atmosphere, at least of any noticeable extent, may well be powerful when a comet approaches the sun, and help to explain an electrified condition of the evaporated matter which would possibly bring it under the sun's repulsive action. We shall have to return to this point in speaking of the solar corona.

A very great advance has been made in our knowledge of the constitution of the sun by the recent work at the Johns Hopkins University by means of photography and concave gratings, in comparing the solar spectrum, under great resolving power, directly with the spectra of the terrestrial elements. Professor Rowland has shown that the lines of thirty-six terrestrial elements at least are certainly present in the solar spectrum, while eight others are doubtful. Fifteen elements, including nitrogen, as it shows itself under an electric discharge in a vacuum tube, have not been found in the solar spectrum. Some ten other elements, inclusive of oxygen, have not yet been compared with the sun's spectrum.

Rowland remarks that of the fifteen elements named as not found in the sun, many are so classed because they have few strong lines, or none at all, in the limit of the solar spectrum as compared by him with the arc. Boron has only two strong lines. The lines of bismuth are compound and too diffuse. Therefore, even in the case of these fifteen elements, there is little evidence that they are really absent from the sun.

It follows that if the whole earth were heated to the temperature of the sun, its spectrum would resemble very closely the solar spectrum.

Rowland has not found any lines common to several elements, and in the case of some accidental coincidences, more accurate investigation reveals some slight difference of wave-length or a common impurity. Further, the relative strength of the lines in the solar spectrum is generally, with a few exceptions, the same as that in the electric arc, so that Rowland considers that his experi-

ments show "very little evidence" of the breaking up of the terrestrial elements in the sun.

Stas, in a recent paper, gives the final results of eleven years of research on the chemical elements in a state of purity, and on the possibility of decomposing them by the physical and chemical forces at our disposal. His experiments on calcium, strontium, lithium, magnesium, silver, sodium, and thallium, show that these substances retain their individuality under all conditions, and are unalterable by any forces that we can bring to bear upon them.

Professor Rowland looks to the solar lines which are unaccounted for as a means of enabling him to discover such new terrestrial elements as still lurk in rare minerals and earths, by confronting their spectra directly with that of the sun. He has already resolved yttrium spectroscopically into three components, and actually into two. The comparison of the results of this independent analytical method with the remarkable but different conclusions to which M. Lecoq de Boisbaudran and Mr. Crookes have been led respectively, from spectroscopic observation of these bodies when glowing under molecular bombardment in a vacuum tube, will be awaited with much interest. It is worthy of remark that as our knowledge of the spectrum of hydrogen in its complete form came to us from the stars, it is now from the sun that chemistry is probably about to be enriched by the discovery of new elements.

In a discussion in the Bakerian lecture for 1885 of what we knew up to that time of the sun's corona, I was led to the conclusion that the corona is essentially a phenomenon similar in the cause of its formation to the tails of comets, namely, that it consists for the most part probably of matter going from the sun under the action of a force, possibly electrical, which varies as the surface, and can therefore in the case of highly attenuated matter, easily master the force of gravity even near the sun. Though many of the coronal particles may return to the sun, those which form the long rays or streamers do not return; they separate, and soon become too diffused to be any longer visible, and may well go to furnish the matter of the zodiacal light, which otherwise has not received a satisfactory explanation. And further, if such a force exist at the sun, the changes of terrestrial magnetism may be due to direct electric action, as the earth moves through lines of inductive force.

These conclusions appear to be in accordance broadly with the lines along which thought has been directed by the results of subsequent eclipses. Professor Schuster takes an essentially similar view, and suggests that there may be a direct electric connection between the sun and the planets. He asks further whether the sun may not act like a magnet in consequence of its revolution about its axis. Professor Bigelow has recently treated the coronal forms by the theory of spherical harmonics, on the supposition that we see phenomena similar to those of free electricity, the rays being lines of force, and the coronal matter discharged from the sun, or at least arranged or controlled by these forces. At the extremities of the streams for some reasons the repulsive power may be lost, and gravitation set in, bringing the matter back to the sun. The matter which does leave the sun is persistently transported to the equatorial plane of the corona; in fact, the zodiacal light may be the accumulation at great distances from the sun along this equator of such like material. Photographs on a larger scale will be desirable for the full development of the conclusions which may follow from this study of the curved forms of the coronal structure. Professor Schaeberle, however, considers that the coronal phenomena may be satisfactorily accounted for on the supposition that the corona is formed of streams of matter ejected mainly from the spot zones with great initial velocities, but smaller than 382 miles a second. Further, that the different types of the corona are due to the effects of perspective on the streams from the earth's place at the time relatively to the plane of the solar equator.

Of the physical and the chemical nature of the coronal matter we know very little. Schuster concludes, from an examination of the eclipses of 1882, 1883, and 1886, that the continuous spectrum of the corona has the maximum of actinic intensity displaced considerably towards the red when compared with the spectrum of the sun, which shows that it can only be due in small part to solar light scattered by small particles. The lines of calcium and of hydrogen do not appear to form part of the normal spectrum of the corona. The green coronal line has no known representative in terrestrial substances, nor has Schuster been able to recognise any of our elements in the other lines of the corona.

The spectra of the stars are almost infinitely diversified, yet they can be arranged with some exceptions in a series in which the adjacent spectra, especially in the photographic region, are scarcely distinguishable, passing from the bluish-white stars like Sirius, through stars more or less solar in character, to stars with banded spectra, which divide themselves into two apparently independent groups according as the stronger edge of the bands is towards the red or the blue. In such an arrangement the sun's place is towards the middle of the series.

At present a difference of opinion exists as to the direction in the series in which evolution is proceeding, whether by further condensation white stars pass into the orange and red stages, or whether these more coloured stars are younger, and will become white by increasing age. The latter view was suggested by Johnstone Stoney in 1867.

About ten years ago Ritter, in a series of papers, discussed the behaviour of gaseous masses during condensation, and the probable resulting constitution of the heavenly bodies. According to him a star passes through the orange and red stages twice, first during a comparatively short period of increasing temperature which culminates in the white stage, and a second time during a more prolonged stage of gradual cooling. He suggested that the two groups of banded stars may correspond to these different periods: the young stars being those in which the stronger edge of the dark band is towards the blue, the other banded stars, which are relatively less luminous and few in number, being those which are approaching extinction through age.

Recently a similar evolutionary order has been suggested, which is based upon the hypothesis that the nebulae and stars consist of colliding meteoric stones in different stages of condensation.

More recently the view has been put forward that the diversified spectra of the stars do not represent the stages of an evolutionary progress, but are due for the most part to differences of original constitution.

The few minutes which can be given to this part of the address are insufficient for a discussion of these different views. I purpose, therefore, to state briefly, and with reserve as the subject is obscure, some of the considerations from the characters of their spectra which appeared to me to be in favour of the evolutionary order in which I arranged the stars from their photographic spectra in 1879. This order is essentially the same as Vogel had previously proposed in his classification of the stars in 1874, in which the white stars, which are most numerous, represent the early adult and most persistent stage of stellar life, the solar condition that of full maturity and of commencing age; while in the orange and red stars with banded spectra we see the setting in and advance of old age. But this statement must be taken broadly, and not as asserting that all stars, however different in mass and possibly to some small extent in original constitution, exhibit one invariable succession of spectra.

In the spectra of the white stars the dark metallic lines are relatively inconspicuous, and occasionally absent, at the same time that the dark lines of hydrogen are usually strong, and more or less broad, upon a continuous spectrum, which is remarkable for its brilliancy at the blue end. In

some of these stars the hydrogen and some other lines are bright, and sometimes variable.

As the greater or less prominence of the hydrogen lines, dark or bright, is characteristic of the white stars as a class, and diminishes gradually with the incoming and increase in strength of the other lines, we are probably justified in regarding it as due to some conditions which occur naturally during the progress of stellar life, and not to a peculiarity of original constitution.

To produce a strong absorption-spectrum a substance must be at the particular temperature at which it is notably absorptive; and, further, this temperature must be sufficiently below that of the region behind from which the light comes for the gas to appear, so far as its special rays are concerned, as darkness upon it. Considering the high temperature to which hydrogen must be raised before it can show its characteristic emission and absorption, we shall probably be right in attributing the relative feebleness or absence of the other lines, not to the paucity of the metallic vapours, but rather to their being so hot relatively to the substances behind them as to show feebly, if at all, by reversion. Such a state of things would more probably be found, it seems to me, in conditions anterior to the solar stage. A considerable cooling of the sun would probably give rise to banded spectra due to compounds, or to more complex molecules, which might form near the condensing points of the vapours.

The sun and stars are generally regarded as consisting of glowing vapours surrounded by a photosphere where condensation is taking place, the temperature of the photospheric layer from which the greater part of the radiation comes being constantly renewed from the hotter matter within.

At the surface the convection currents would be strong, producing a considerable commotion, by which the different gases would be mixed and not allowed to retain the inequality of proportions at different levels due to their vapour densities.

Now the conditions of the radiating photosphere and those of the gases above it, on which the character of the spectrum of a star depends, will be determined, not alone by temperature, but also by the force of gravity in these regions; this force will be fixed by the star's mass and its stage of condensation, and will become greater as the star continues to condense.

In the case of the sun the force of gravity has already become so great at the surface that the decrease of the density of the gases must be extremely rapid, passing in the space of a few miles from atmospheric pressure to a density infinitesimally small; consequently the temperature gradient at the surface, if determined solely by expansion, must be extremely rapid. The gases here, however, are exposed to the fierce radiation of the sun, and unless wholly transparent would take up heat, especially if any solid or liquid particles were present from condensation or convection currents.

From these causes, within a very small extent of space at the surface of the sun, all bodies with which we are acquainted should fall to a condition in which the extremely tenuous gas could no longer give a visible spectrum. The insignificance of the angle subtended by this space as seen from the earth should cause the boundary of the solar atmosphere to appear defined. If the boundary which we see be that of the sun proper, the matter above it will have to be regarded as in an essentially dynamical condition—an assemblage, so to speak, of gaseous projectiles for the most part falling back upon the sun after a greater or less range of flight. But in any case it is within a space of relatively small extent in the sun, and probably in the other solar stars, that the reversion which is manifested by dark lines is to be regarded as taking place.

Passing backward in the star's life, we should find a gradual weakening of gravity at the surface, a reduction of the temperature gradient so far as it was determined by expansion, and convection currents of less violence

producing less interference with the proportional quantities of gases due to their vapour densities, while the effects of eruptions would be more extensive.

At last we might come to a state of things in which, if the star were hot enough, only hydrogen might be sufficiently cool relatively to the radiation behind to produce a strong absorption. The lower vapours would be protected, and might continue to be relatively too hot for their lines to appear very dark upon the continuous spectrum; besides, their lines might be possibly to some extent effaced by the coming in under such conditions in the vapours themselves of a continuous spectrum.

In such a star the light radiated towards the upper part of the atmosphere may have come from portions lower down of the atmosphere itself, or at least from parts not greatly hotter. There may be no such great difference of temperature of the low and less low portions of the star's atmosphere as to make the darkening effect of absorption of the protected metallic vapours to prevail over the illuminating effect of their emission.

It is only by a vibratory motion corresponding to a very high temperature that the bright lines of the first spectrum of hydrogen can be brought out, and by the equivalence of absorbing and emitting power that the corresponding spectrum of absorption should be produced; yet for a strong absorption to show itself, the hydrogen must be cool relatively to the source of radiation behind it, whether this be condensed particles or gas. Such conditions, it seems to me, should occur in the earlier rather than in the more advanced stages of condensation.

The subject is obscure, and we may go wrong in our mode of conceiving of the probable progress of events, but there can be no doubt that in one remarkable instance the white-star spectrum is associated with an early stage of condensation.

Sirius is one of the most conspicuous examples of one type of this class of stars. Photometric observations combined with its ascertained parallax show that this star emits from forty to sixty times the light of our sun, even to the eye, which is insensible to ultra-violet light, in which Sirius is very rich, while we learn from the motion of its companion that its mass is not much more than double that of our sun. It follows that, unless we attribute to this star an improbably great emissive power, it must be of immense size, and in a much more diffuse and therefore an earlier condition than our sun; though probably at a later stage than those white stars in which the hydrogen lines are bright.

A direct determination of the relative temperature of the photospheres of the stars might possibly be obtained in some cases from the relative position of maximum radiation of their continuous spectra. Langley has shown that through the whole range of temperature on which we can experiment, and presumably at temperatures beyond, the maximum of radiation power in solid bodies gradually shifts upwards in the spectrum from the infra-red through the red and orange, and that in the sun it has reached the blue.

The defined character as a rule of the stellar lines of absorption suggests that the vapours producing them do not at the same time exert any strong power of general absorption. Consequently we should probably not go far wrong, when the photosphere consists of liquid or solid particles, if we could compare select parts of the continuous spectrum between the stronger lines or where they are fewest. It is obvious that if extended portions of different stellar spectra were compared, their true relation would be obscured by the line-absorption.

The increase of temperature, as shown by the rise in the spectrum of the maximum of radiation, may not always be accompanied by a corresponding greater brightness of a star as estimated by the eye, which is an extremely imperfect photometric instrument. Not only is the eye blind to large regions of radiation, but even for the small range of light that we can see the visual effect varies enormously with its colour. According to Prof.

Langley, the same amount of energy which just enables us to perceive light in the crimson at A would in the green produce a visual effect 100,000 times greater. In the violet the proportional effect would be 1,600, in the blue 62,000, in the yellow 28,000, in the orange 14,000, and in the red 1,200. Captain Abney's recent experiments make the sensitiveness of the eye for the green near F to be 750 times greater than for red about C. It is for this reason, at least in part, that I suggested in 1864, and have since shown by direct observation, that the spectrum of the nebula in Andromeda, and presumably of similar nebulae, is in appearance only wanting in the red.

The stage at which the maximum radiation is in the green, corresponding to the eye's greatest sensitiveness, would be that in which it could be most favourably measured by eye-photometry. As the maximum rose into the violet and beyond, the star would increase in visual brightness, but not in proportion to the increase of energy radiated by it.

The brightness of a star would be affected by the nature of the substance by which the light was chiefly emitted. In the laboratory solid carbon exhibits the highest emissive power. A stellar stage in which radiation comes, to a large extent, from a photosphere of the solid particles of this substance, would be favourable for great brilliancy. Though the stars are built up of matter essentially similar to that of the sun, it does not follow that the proportion of the different elements is everywhere the same. It may be that the substances condensed in the photospheres of different stars may differ in their emissive powers, but probably not to a great extent.

All the heavenly bodies are seen by us through the tinted medium of our atmosphere. According to Langley, the solar stage of stars is not really yellow, but, even as gauged by our imperfect eyes, would appear bluish-white if we could free ourselves from the deceptive influences of our surroundings.

From these considerations it follows that we can scarcely infer the evolutionary stages of the stars from a simple comparison of their eye-magnitudes. We should expect the white stars to be, as a class, less dense than the stars in the solar stage. As great mass might bring in the solar type of spectrum at a relatively earlier time, some of the brightest of these stars may be very massive and brighter than the sun—for example, the brilliant star Arcturus. For these reasons the solar stars should not only be denser than the white stars, but perhaps, as a class, surpass them in mass and eye-brightness.

It has been shown by Lane that, so long as a condensing gaseous mass remains subject to the laws of a purely gaseous body, its temperature will continue to rise.

The greater or less breadth of the lines of absorption of hydrogen in the white stars may be due to variations of the depth of the hydrogen in the line of sight, arising from the causes which have been discussed. At the sides of the lines the absorption and emission are feeble than in the middle, and would come out more strongly with a greater thickness of gas.

The diversities among the white stars are nearly as numerous as the individuals of the class. Time does not permit me to do more than to record that, in addition to the three sub-classes into which they have been divided by Vogel, Scheiner has recently investigated minor differences as suggested by the character of the third line of hydrogen near G. He has pointed out, too, that so far as his observations go the white stars in the constellation of Orion stand alone, with the exception of Algol, in possessing a dark line in the blue which has apparently the same position as a bright line in the great nebula of the same constellation; and Pickering finds, in his photographs of the spectra of these stars, dark lines corresponding to the principal lines of the bright-line stars, and the planetary nebulae, with the exception of the chief nebular line. The association of white stars with nebular matter in Orion, in the Pleiades, in

the region of the Milky Way, and in other parts of the heavens, may be regarded as falling in with the view that I have taken.

In the stars possibly further removed from the white class than our sun, belonging to the first division of Vogel's third class, which are distinguished by absorption bands with their stronger edge towards the blue, the hydrogen lines are narrower than in the solar spectrum. In these stars the density gradient is probably still more rapid, the depth of hydrogen may be less, and possibly the hydrogen molecules may be affected by a larger number of encounters with dissimilar molecules. In some red stars with dark hydrocarbon bands the hydrogen lines have not been certainly observed; if they are really absent, it may be because the temperature has fallen below the point at which hydrogen can exert its characteristic absorption; besides, some hydrogen will have united with the carbon. The coming in of the hydrocarbon bands may indicate a later evolutionary stage, but the temperature may still be high, as acetylene can exist in the electric arc.

A number of small stars, more or less similar to those which are known by the names of their discoverers, Wolf and Rayet, have been found by Pickering in his photographs. These are remarkable for several brilliant groups of bright lines, including frequently the hydrogen lines and the line D_3 , upon a continuous spectrum strong in blue and violet rays, in which are also dark lines of absorption. As some of the bright groups appear in his photographs to agree in position with corresponding bright lines in the planetary nebulae, Pickering suggests that these stars should be placed in one class with them, but the brightest nebular line is absent from these stars. The simplest conception of their nature would be that each star is surrounded by a nebula, the bright groups being due to the gaseous matter outside the star. Mr. Roberts, however, has not been able to bring out any indication of nebulosity by prolonged exposure. The remarkable star η Argus may belong to this class of the heavenly bodies.

In the nebulae, the elder Herschel saw portions of the fiery mist or "shining fluid" out of which the heavens and the earth had been slowly fashioned. For a time this view of the nebulae gave place to that which regarded them as external galaxies, cosmical "sandheaps," too remote to be resolved into separate stars; though indeed, in 1858, Mr. Herbert Spencer showed that the observations of nebulae up to that time were really in favour of an evolutionary progress.

In 1864 I brought the spectroscope to bear upon them; the bright lines which flashed upon the eye showed the source of the light to be glowing gas, and so restored these bodies to what is probably their true place, as an early stage of sidereal life.

At that early time our knowledge of stellar spectra was small. For this reason partly, and probably also under the undue influence of theological opinions then widely prevalent, I unwisely wrote in my original paper, in 1864, "that in these objects we no longer have to do with a special modification of our own type of sun, but find ourselves in presence of objects possessing a distinct and peculiar plan of structure." Two years later, however, in a lecture before this Association, I took a truer position. "Our views of the universe," I said, "are undergoing important changes; let us wait for more facts with minds unfettered by any dogmatic theory, and therefore free to receive the teaching, whatever it may be, of new observations."

Let us turn aside for a moment from the nebulae in the sky to the conclusions to which philosophers had been irresistibly led by a consideration of the features of the solar system. We have before us in the sun and planets obviously not a haphazard aggregation of bodies, but a system resting upon a multitude of relations pointing to a common physical cause. From these considerations

Kant and Laplace formulated the nebular hypothesis, resting it on gravitation alone, for at that time the science of the conservation of energy was practically unknown. These philosophers showed how, on the supposition that the space now occupied by the solar system was once filled by a vaporous mass, the formation of the sun and planets could be reasonably accounted for.

By a totally different method of reasoning, modern science traces the solar system backward step by step to a similar state of things at the beginning. According to Helmholtz the sun's heat is maintained by the contraction of his mass, at the rate of about 220 feet a year. Whether at the present time the sun is getting hotter or colder we do not certainly know. We can reason back to the time when the sun was sufficiently expanded to fill the whole space occupied by the solar system, and was reduced to a great glowing nebula. Though man's life—the life of the race perhaps—is too short to give us direct evidence of any distinct stages of so august a process, still the probability is great that the nebular hypothesis, especially in the more precise form given to it by Roche, does represent broadly, notwithstanding some difficulties, the succession of events through which the sun and planets have passed.

The nebular hypothesis of Laplace requires a rotating mass of fluid which at successive epochs became unstable from excess of motion, and left behind rings, or more probably perhaps lumps, of matter from the equatorial regions.

The difficulties to which I have referred have suggested to some thinkers a different view of things, according to which it is not necessary to suppose that one part of the system gravitationally supports another. The whole may consist of a congeries of discrete bodies, even if these bodies be the ultimate molecules of matter. The planets may have been formed by the gradual accretion of such discrete bodies. On the view that the material of the condensing solar system consisted of separate particles or masses, we have no longer the fluid pressure which is an essential part of Laplace's theory. Faye, in his theory of evolution from meteorites, has to throw over this fundamental idea of the nebular hypothesis, and he formulates instead a different succession of events in which the outer planets were formed last—a theory which has difficulties of its own.

Professor George Darwin has recently shown, from an investigation of the mechanical conditions of a swarm of meteorites, that on certain assumptions a meteoric swarm might behave as a coarse gas, and in this way bring back the fluid pressure exercised by one part of the system on the other, which is required by Laplace's theory. One chief assumption consists in supposing that such inelastic bodies as meteoric stones might attain the effective elasticity of a high order which is necessary to the theory through the sudden volatilisation of a part of their mass at an encounter, by which what is virtually a violent explosive is introduced between the two colliding stones. Professor Darwin is careful to point out that it must necessarily be obscure as to how a small mass of solid matter can take up a very large amount of energy in a small fraction of a second.

Any direct indications from the heavens themselves, however slight, are of so great value that I should perhaps in this connection call attention to a recent remarkable photograph, by Mr. Roberts, of the great nebula in Andromeda. On this plate we seem to have presented to us some stage of cosmical evolution, on a gigantic scale. The photograph shows a sort of whirlpool disturbance of the luminous matter which is distributed in a plane inclined to the line of sight, in which a series of rings of bright matter separated by dark spaces, greatly foreshortened by perspective, surround a large undefined central mass. We are ignorant of the parallax of this nebula, but there can be little doubt that we are looking upon a system very remote, and therefore of a magnitude great beyond our power of adequate comprehension.

The matter of this nebula, in whatever state it may be, appears to be distributed, as in so many other nebulae, in rings or spiral streams, and to suggest a stage in a succession of evolutionary events not inconsistent with that which the nebular hypothesis requires. To liken this object more directly to any particular stage in the formation of the solar system would be "to compare things great with small," and might be indeed to introduce a false analogy; but, on the other hand, we should err through an excess of caution if we did not accept the remarkable features brought to light by this photograph as a presumptive indication of a progress of events in cosmical history following broadly upon the lines of Laplace's theory.

The old view of the original matter of the nebulae, that it consisted of a "fiery mist,"—

"a tumultuous cloud
Instinct with fire and nitre,"

fell at once with the rise of the science of thermodynamics. In 1854 Helmholtz showed that the supposition of an original fiery condition of the nebulous stuff was unnecessary, since in the mutual gravitation of widely separated matter we have a store of potential energy sufficient to generate the high temperature of the sun and stars. We can scarcely go wrong in attributing the light of the nebulae to the conversion of the gravitational energy of shrinkage into molecular motion.

The idea that the light of comets and of nebulae may be due to a succession of ignited flashes of gas from the encounters of meteoric stones was suggested by Professor Tait, and was brought to the notice of this Association in 1871 by Sir William Thomson in his Presidential Address.

The spectrum of the bright-line nebulae is certainly not such a spectrum as we should expect from the flashing by collisions of meteorites similar to those which have been analysed in our laboratories. The strongest lines of the substances which in the case of such meteorites would first show themselves—iron, sodium, magnesium, nickel, &c.—are not those which distinguish the nebular spectrum. On the contrary, this spectrum is chiefly remarkable for a few brilliant lines, very narrow and defined, upon a background of a faint continuous spectrum, which contains numerous bright lines, and probably some lines of absorption.

The two most conspicuous lines have not been interpreted; for though the second line falls near, it is not coincident with a strong double line of iron. It is hardly necessary to say that though the near position of the brightest line to the bright double line of nitrogen, as seen in a small spectroscopic in 1864, naturally suggested at that early time the possibility of the presence of this element in the nebulae, I have been careful to point out, to prevent misapprehension, that in more recent years the nitrogen line and subsequently a lead line have been employed by me solely as fiducial points of reference in the spectrum.

The third line we know to be the second line of the first spectrum of hydrogen. Mr. Keeler has seen the first hydrogen line in the red, and photographs show that this hydrogen spectrum is probably present in its complete form, or nearly so, as we first learnt to know it in the absorption spectrum of the white stars.

We are not surprised to find associated with it the line D_3 , near the position of the absent sodium lines, probably due to the atom of some unknown gas, which in the sun can only show itself in the outbursts of highest temperature, and for this reason does not reveal itself by absorption in the solar spectrum.

It is not unreasonable to assume that the two brightest lines, which are of the same order, are produced by substances of a similar nature, in which a vibratory motion corresponding to a very high temperature is also necessary. These substances, as well as that represented by the line D_3 , may be possibly some of the unknown elements which are wanting in our terrestrial chemistry

between hydrogen and lithium, unless indeed D_3 be on the lighter side of hydrogen.

In the laboratory we must have recourse to the electric discharge to bring out the spectrum of hydrogen; but in a vacuum tube, though the radiation may be great, from the relative fewness of the luminous atoms or molecules, or from some other cause, the temperature of the gas as a whole may be low.

On account of the large extent of the nebulae, a comparatively small number of luminous molecules or atoms would probably be sufficient to make the nebulae as bright as they appear to us. On such an assumption the average temperature may be low, but the individual particles, which by their encounters are luminous, must have motions corresponding to a very high temperature, and in this sense be extremely hot.

In such diffuse masses, from the great mean length of free path, the encounters would be rare but correspondingly violent, and tend to bring about vibrations of comparatively short period, as appears to be the case if we may judge by the great relative brightness of the more refrangible lines of the nebular spectrum.

Such a view may perhaps reconcile the high temperature which the nebular spectrum undoubtedly suggests with the much lower mean temperature of the gaseous mass, which we should expect at so early a stage of condensation, unless we assume a very enormous mass; or that the matter coming together had previously considerable motion, or considerable molecular agitation.

The inquisitiveness of the human mind does not allow us to remain content with the interpretation of the present state of the cosmical masses, but suggests the question—

"What see'st thou else
In the dark backward and abyss of time?"

What was the original state of things? how has it come about that, by the side of ageing worlds, we have nebulae in a relatively younger stage? Have any of them received their birth from dark suns, which have collided into new life, and so belong to a second or later generation of the heavenly bodies?

During the short historic period, indeed, there is no record of such an event; still it would seem to be only through the collision of dark suns, of which the number must be increasing, that a temporary rejuvenescence of the heavens is possible, and by such ebbings and flowings of stellar life that the inevitable end to which evolution in its apparently uncompensated progress is carrying us can, even for a little, be delayed.

We cannot refuse to admit as possible such an origin for nebulae.

In considering, however, the formation of the existing nebulae, we must bear in mind that, in the part of the heavens within our ken, the stars still in the early and middle stages of evolution exceed greatly in number those which appear to be in an advanced condition of condensation. Indeed we find some stars which may be regarded as not far advanced beyond the nebular condition.

It may be that the cosmical bodies which are still nebulous owe their later development to some conditions of the part of space where they occur, such as conceivably a greater original homogeneity, in consequence of which condensation began less early. In other parts of space condensation may have been still further delayed, or even have not yet begun. It is worthy of remark that these nebulae group themselves about the Milky Way, where we find a preponderance of the white-star type of stars, and almost exclusively the bright-line stars which Pickering associates with the planetary nebulae. Further, Dr. Gill concludes, from the rapidity with which they impress themselves upon the plate, that the fainter stars of the Milky Way also, to a large extent, belong to this early type of stars. At the same time other types of stars occur also over this region, and the red hydrocarbon stars are found in certain parts; but possibly these stars

may be before or behind the Milky Way, and not physically connected with it.

If light matter be suggested by the spectrum of these nebulae, it may be asked further, as a pure speculation, whether in them we are witnessing possibly a later condensation of the light matter which had been left behind, at least in a relatively greater proportion, after the first growth of worlds into which the heavier matter condensed, though not without some entanglement of the lighter substances. The wide extent and great diffuseness of this bright-line nebulosity over a large part of the constellation of Orion may be regarded perhaps as pointing in this direction. The diffuse nebulous matter streaming round the Pleiades may possibly be another instance, though the character of its spectrum has not yet been ascertained.

In the planetary nebulae, as a rule, there is a sensible increase of the faint continuous spectrum, as well as a slight thickening of the bright lines towards the centre of the nebula, appearances which are in favour of the view that these bodies are condensing gaseous masses.

Professor G. Darwin, in his investigation of the equilibrium of a rotating mass of fluid, found, in accordance with the independent researches of Poincaré, that when a portion of the central body becomes detached through increasing angular velocity, the portion should bear a far larger ratio to the remainder than is observed in the planets and satellites of the solar system, even taking into account heterogeneity from the condensation of the parent mass.

Now this state of things, in which the masses though not equal are of the same order, does seem to prevail in many nebulae, and to have given birth to a large class of binary stars. Mr. See has recently investigated the evolution of bodies of this class, and points out their radical differences from the solar system in the relatively large mass-ratios of the component bodies, as well as in the high eccentricities of their orbits brought about by tidal friction, which would play a more important part in the evolution of such systems.

Considering the large number of these bodies, he suggests that the solar system should perhaps no longer be regarded as representing celestial evolution in its normal form—

"A goodly Paternie to whose perfect mould
He fashioned them" . . .

but rather as modified by conditions which are exceptional.

It may well be that, in the very early stages, condensing masses are subject to very different conditions, and that condensation may not always begin at one or two centres, but sometimes set in at a large number of points, and proceed in the different cases along very different lines of evolution.

Besides its more direct use in the chemical analysis of the heavenly bodies, the spectroscope has given to us a great and unexpected power of advance along the lines of the older astronomy. In the future a higher value may, indeed, be placed upon this indirect use of the spectroscope than upon its chemical revelations.

By no direct astronomical methods could motions of approach or of recession of the stars be even detected, much less could they be measured. A body coming directly towards us or going directly from us appears to stand still. In the case of the stars we can receive no assistance from change of size or of brightness. The stars show no true discs in our instruments, and the nearest of them is so far off that if it were approaching us at the rate of a hundred miles in a second of time, a whole century of such rapid approach would not do more than increase its brightness by the one-fortieth part.

Still it was only too clear that, so long as we were unable to ascertain directly those components of the stars' motions which lie in the line of sight, the speed and direction of the solar motion in space, and many of

the great problems of the constitution of the heavens, must remain more or less imperfectly known. Now the spectroscope has placed in our hands this power, which, though so essential, appeared almost in the nature of things to lie for ever beyond our grasp; it enables us to measure directly, and under favourable circumstances to within a mile per second, or even less, the speed of approach or of recession of a heavenly body. This method of observation has the great advantage for the astronomer of being independent of the distance of the moving body, and is therefore as applicable and as certain in the case of a body on the extreme confines of the visible universe, so long as it is bright enough, as in the case of a neighbouring planet.

Doppler had suggested as far back as 1841 that the same principle, on which he had shown that a sound should become sharper or flatter if there were an approach or a recession between the ear and the source of the sound, would apply equally to light; and he went on to say that the difference of colour of some of the binary stars might be produced in this way by their motions. Doppler was right in that the principle is true in the case of light, but he was wrong in the particular conclusion which he drew from it. Even if we suppose a star to be moving with a sufficiently enormous velocity to alter sensibly its colour to the eye, no such change would actually be seen, for the reason that the store of invisible light beyond both limits of the visible spectrum, the blue and the red, would be drawn upon, and light-waves invisible to us would be exalted or degraded so as to take the place of those raised or lowered in the visible region, and the colour of the star would remain unchanged. About eight years later Fizeau pointed out the importance of considering the individual wave-lengths of which white light is composed. As soon, however, as we had learned to recognise the lines of known substances in the spectra of the heavenly bodies, Doppler's principle became applicable as the basis of a new and most fruitful method of investigation. The measurement of the small shift of the celestial lines from their true positions, as shown by the same lines in the spectrum of a terrestrial substance, gives to us the means of ascertaining directly in miles per second the speed of approach or of recession of the heavenly body from which the light has come.

An account of the first application of this method of research to the stars, which was made in my observatory in 1868, was given by Sir Gabriel Stokes from this chair, at the meeting at Exeter, in 1869. The stellar motions determined by me were shortly after confirmed by Prof. Vogel in the case of Sirius, and in case of other stars by Mr. Christie, now Astronomer Royal, at Greenwich; but, necessarily, in consequence of the inadequacy of the instruments then in use for so delicate an inquiry, the amounts of these motions were but approximate.

The method was shortly afterwards taken up systematically at Greenwich and at the Rugby Observatory. It is to be greatly regretted that, for some reasons, the results have not been sufficiently accordant and accurate for a research of such exceptional delicacy. On this account probably, as well as that the spectroscope at that early time had scarcely become a familiar instrument in the observatory, astronomers were slow in availing themselves of this new and remarkable power of investigation. That this comparative neglect of so truly wonderful a method of ascertaining what was otherwise outside our powers of observation, has greatly retarded the progress of astronomy during the last fifteen years, is but too clearly shown by the brilliant results which within the last couple of years have followed fast upon the recent masterly application of this method by photography at Potsdam, and by eye with the needful accuracy at the Lick Observatory. At last this use of the spectroscope has taken its true place as one of the most potent methods of astronomical research. It gives us the motions of approach and of recession, not in angular measures which depend for their translation into actual velocities upon

separate determinations of parallax displacements, but at once in terrestrial units of distance.

This method of work will doubtless be very prominent in the astronomy of the near future, and to it probably we shall have to look for the more important discoveries in sidereal astronomy which will be made during the coming century.

In his recent application of photography to this method of determining celestial motions, Professor Vogel, assisted by Dr. Scheiner, considering the importance of obtaining the spectrum of as many stars as possible on an extended scale without an exposure inconveniently long, wisely determined to limit the part of the spectrum on the plate to the region for which the ordinary silver-bromide gelatine plates are most sensitive, namely, to a small distance on each side of G, and to employ as the line of comparison the hydrogen line near G, and recently also certain lines of iron. The most minute and complete mechanical arrangements were provided for the purpose of securing the absolute rigidity of the comparison spectrum relatively to that of the star, and for permitting temperature adjustments and other necessary ones to be made.

The perfection of these spectra is shown by the large number of lines, no fewer than 250 in the case of Capella, within the small region of the spectrum on the plate. Already the motions of about fifty stars have been measured with an accuracy, in the case of the larger number of them, of about an English mile per second.

At the Lick Observatory it has been shown that observations can be made directly by eye with an accuracy equally great. Mr. Keeler's brilliant success has followed in great measure from the use of the third and fourth spectra of a grating 14,438 lines to the inch. The marvellous accuracy attainable in his hands on a suitable star, is shown by observations on three nights of the star Arcturus, the largest divergence of his measures being not greater than six-tenths of a mile per second, while the mean of the three nights' work agreed with the mean of five photographic determinations of the same star at Potsdam to within one tenth of an English mile. These are determinations of the motions of a sun so stupendously remote that even the method of parallax practically fails to fathom the depth of intervening space, and by means of light-waves which have been, according to Elkin's nominal parallax, nearly 200 years upon their journey.

Mr. Keeler, with his magnificent means, has accomplished a task which I attempted in vain in 1874, with the comparatively poor appliances at my disposal, of measuring the motions in the line of sight of some of the planetary nebulae. As the stars have considerable motions in space it was to be expected that nebulae should possess similar motions, for the stellar motions must have belonged to the nebulae out of which they have been evolved. My instrumental means, limiting my power of detection to motions greater than twenty-five miles per second, were insufficient. Mr. Keeler has found in the examination of ten nebulae motions varying from two miles to twenty-seven miles, with one exceptional motion of nearly forty miles.

For the nebula of Orion Mr. Keeler finds a motion of recession of about ten miles a second. Now this motion agrees closely with what it should appear to have from the drift of the solar system itself, so far as it has been possible at present to ascertain the probable velocity of the sun in space. This grand nebula, of vast extent and of extreme tenuity, is probably more nearly at rest relatively to the stars of our system than any other celestial object we know; still, it would seem more likely than even here we have some motion, small though it may be, than that the motions of the matter of which it is formed were so absolutely balanced as to leave this nebula in the unique position of absolute immobility in the midst of whirling and drifting suns and systems of suns.

The spectroscopic method of determining celestial

motions in the line of sight has recently become fruitful in a new but not altogether unforeseen direction, for it has, so to speak, given us a separating power far beyond that of any telescope the glass-maker and the optician could construct, and so enabled us to penetrate into mysteries hidden in stars apparently single, and altogether unsuspected of being binary systems. The spectroscope has not simply added to the list of the known binary stars, but has given to us for the first time a knowledge of a new class of stellar systems, in which the components are in some cases of nearly equal magnitude, and in close proximity, and are revolving with velocities greatly exceeding the planetary velocities of our system.

The K line in the photographs of Mizar, taken at the Harvard College Observatory, was found to be double at intervals of fifty-two days. The spectrum was therefore not due to a single source of light, but to the combined effect of two stars moving periodically in opposite directions in the line of sight. It is obvious that if two stars revolve round their common centre of gravity in a plane not perpendicular to the line of sight, all the lines in a spectrum common to the two stars will appear alternately single or double.

In the case of Mizar and the other stars to be mentioned, the spectroscopic observations are not as yet extended enough to furnish more than an approximate determination of the elements of their orbits.

Mizar especially, on account of its relatively long period, about 105 days, needs further observations. The two stars are moving each with a velocity of about fifty miles a second, probably in elliptical orbits, and are about 143 millions of miles apart. The stars of about equal brightness have together a mass about forty times as great as that of our sun.

A similar doubling of the lines showed itself in the Harvard photographs of β Aurigæ at the remarkably close interval of almost exactly two days, indicating a period of revolution of about four days. According to Vogel's later observations, each star has a velocity of nearly seventy miles a second, the distance between the stars being little more than seven and a half millions of miles, and the mass of the system 4.7 times that of the sun. The system is approaching us at the speed of about sixteen miles a second.

The telescope could never have revealed to us double stars of this order. In the case of β Aurigæ, combining Vogel's distance with Pritchard's recent determination of the star's parallax, the greatest angular separation of the stars as seen from the earth would be 1-200th part of a second of arc, and therefore very far too small for the highest powers of the largest telescopes. If we take the relation of aperture to separating power usually accepted, an object-glass of about eighty feet in diameter would be needed to resolve this binary star. The spectroscope, which takes no note of distance, magnifies, so to speak, this minute angular separation 4000 times; in other words, the doubling of the lines, which is the phenomenon that we have to observe, amounts to the easily measurable quantity of twenty seconds of arc.

There were known, indeed, variable stars of short period, which it had been suggested might be explained on the hypothesis of a dark body revolving about a bright sun in a few days, but this theory was met by the objection that no such systems of closely revolving suns were known to exist.

The Harvard photographs of which we have been speaking were taken with a slitless form of spectroscope, the prisms being placed, as originally by Fraunhofer, before the object-glass of the telescope. This method, though it possesses some advantages, has the serious drawback of not permitting a direct comparison of the star's spectrum with terrestrial spectra. It is obviously unsuited to a variable star like Algol, where one star only is bright, for in such a case there would be no doubling of the lines, but only a small shift to and fro of the lines of the bright star as it moved on its orbit alternately towards

and from our system, which would need for its detection the fiducial positions of terrestrial lines compared directly with them.

For such observations the Potsdam spectrograph was well adapted. Professor Vogel found that the bright star of Algol did pulsate backwards and forwards in the visual direction in a period corresponding to the known variation of its light. The explanation which had been suggested for the star's variability, that it was partially eclipsed at regular intervals of 68·8 hours by a dark companion large enough to cut off nearly five-sixths of its light, was therefore the true one. The dark companion, no longer able to hide itself by its obscurity, was brought out into the light of direct observation by means of its gravitational effects.

Seventeen hours before minimum Algol is receding at the rate of about 24½ miles a second, while seventeen hours after minimum it is found to be approaching with a speed of about 28½ miles. From these data, together with those of the variation of its light, Vogel found, on the assumption that both stars have the same density, that the companion, nearly as large as the sun, but with about one-fourth his mass, revolves with a velocity of about 55 miles a second. The bright star of about twice the size and mass moves about the common centre of gravity with the speed of about 26 miles a second. The system of the two stars, which are about 3½ millions of miles apart, considered as a whole, is approaching us with a velocity of 2·4 miles a second. The great difference in luminosity of the two stars, not less than fifty times, suggests rather that they are in different stages of condensation, and dissimilar in density.

It is obvious that if the orbit of a star with an obscure companion is inclined to the line of sight, the companion will pass above or below the bright star and produce no variation of its light. Such systems may be numerous in the heavens. In Vogel's photographs, Spica, which is not variable, by a small shifting of its lines reveals a backward and forward periodical pulsation due to orbital motion. As the pair whirl round their common centre of gravity, the bright star is sometimes advancing, at others receding. They revolve in about four days, each star moving with a velocity of about 56 miles a second in an orbit probably nearly circular, and possess a combined mass of rather more than 2½ times that of the sun. Taking the most probable value for the star's parallax, the greatest angular separation of the stars would be far too small to be detected with the most powerful telescopes.

If in a close double star the fainter companion is of the white star type, while the bright star is solar in character, the composite spectrum would be solar with the hydrogen lines unusually strong. Such a spectrum would in itself afford some probability of a double origin, and suggest the existence of a companion star.

In the case of a true binary star the orbital motions of the pair would reveal themselves in a small periodical swaying of the hydrogen lines relatively to the solar ones.

Prof. Pickering considers that his photographs show ten stars with composite spectra; of these, five are known to be double. The others are— γ Persei, ζ Aurigæ, δ Sagittarii, γ Ceti, and β Capricorni. Perhaps β Lyrae should be added to this list.

In his recent classical work on the rotation of the sun, Dunér has not only determined the solar rotation for the equator, but for different parallels of latitude up to 75°. The close accordance of his results shows that these observations are sufficiently accurate to be discussed with the variation of the solar rotation for different latitudes, which had been determined by the older astronomical methods from the observations of the solar spots.

Though I have already spoken incidentally of the invaluable aid which is furnished by photography in some of the applications of the spectroscope to the heavenly bodies, the new power which modern photography has put

into the hands of the astronomer is so great, and has led already, within the last few years, to new acquisitions of knowledge of such vast importance, that it is fitting that a few sentences should be specially devoted to this subject.

Photography is no new discovery, being about half a century old; it may excite surprise, and indeed possibly suggest some apathy on the part of astronomers, that though the suggestion of the application of photography to the heavenly bodies dates from the memorable occasion when, in 1839, Arago, announcing to the Académie des Sciences the great discovery of Niepce and Daguerre, spoke of the possibility of taking pictures of the sun and moon by the new process, yet that it is only within a few years that notable advances in astronomical methods and discovery have been made by its aid.

The explanation is to be found in the comparative unsuitability of the earlier photographic methods for use in the observatory. In justice to the early workers in astronomical photography, among whom Bond, De la Rue, J. W. Draper, Rutherford, Gould, hold a foremost place, it is needful to state clearly that the recent great successes in astronomical photography are not due to greater skill, nor, to any great extent, to superior instruments, but to the very great advantages which the modern gelatine dry plate possesses for use in the observatory over the methods of Daguerre, and even over the wet collodion film on glass which, though a great advance on the silver plate, went but a little way towards putting into the hands of the astronomer a photographic surface adapted fully to his wants.

The modern silver-bromide gelatin plate, except for its grained texture, meets the needs of the astronomer at all points. It possesses extreme sensitiveness; it is always ready for use; it can be placed in any position; it can be exposed for hours; lastly, it does not need immediate development, and for this reason can be exposed again to the same object on succeeding nights, so as to make up by several instalments, as the weather may permit, the total time of exposure which is deemed necessary.

Without the assistance of photography, however greatly the resources of genius might overcome the optical and mechanical difficulties of constructing large telescopes, the astronomer would have to depend in the last resource upon his eye. Now we cannot by the force of continued looking bring into view an object too feebly luminous to be seen at the first and keenest moment of vision. But the feeblest light which falls upon the plate is not lost, but is taken in and stored up continuously. Each hour the plate gathers up 3600 times the light-energy which is received during the first second. It is by this power of accumulation that the photographic plate may be said to increase, almost without limit, though not in separating power, the optical means at the disposal of the astronomer for the discovery or the observation of faint objects.

Two principal directions may be pointed out in which photography is of great service to the astronomer. It enables him within the comparatively short time of a single exposure to secure permanently with great exactness the relative positions of hundreds or even of thousands of stars, or the minute features of nebulae or other objects, or the phenomena of a passing eclipse, a task which by means of the eye and hand could only be accomplished, if done at all, after a very great expenditure of time and labour. Photography puts it in the power of the astronomer to accomplish in the short span of his own life, and so enter into their fruition, great works which otherwise must have been passed on by him as an heritage of labour to succeeding generations.

The second great service which photography renders is not simply an aid to the powers the astronomer already possesses. On the contrary, the plate, by recording light-waves which are both too small and too large to excite vision in the eye, brings him into a new region of knowledge, such as the infra-red and the ultra-violet parts of

the spectrum, which must have remained for ever unknown but for artificial help.

The present year will be memorable in astronomical history for the practical beginning of the Photographic Chart and Catalogue of the Heavens, which took their origin in an International Conference which met in Paris in 1887, by the invitation of M. l'Amiral Mouchez, Director of the Paris Observatory.

The richness in stars down to the ninth magnitude of the photographs of the comet of 1882 taken at the Cape Observatory under the superintendence of Dr. Gill, and the remarkable star charts of the Brothers Henry which followed two years later, astonished the astronomical world. The great excellence of these photographs, which was due mainly to the superiority of the gelatine plate, suggested to these astronomers a complete map of the sky, and a little later gave birth in the minds of the Paris astronomers to the grand enterprise of an International Chart of the Heavens. The actual beginning of the work this year is in no small degree due to the great energy and tact with which the Director of the Paris Observatory has conducted the initial steps, through the many delicate and difficult questions which have unavoidably presented themselves in an undertaking which depends upon the harmonious working in common of many nationalities, and of no fewer than eighteen observatories in all parts of the world. The three years since 1887 have not been too long for the detailed organisation of this work, which has called for several elaborate preliminary investigations on special points in which our knowledge was insufficient, and which have been ably carried out by Professors Vogel and Bakhuyzen, Dr. Trépied, Dr. Scheiner, Dr. Gill, the Astronomer Royal, and others. Time also was required for the construction of the new and special instruments.

The decisions of the Conference in their final form provide for the construction of a great photographic chart of the heavens with exposures corresponding to forty minutes' exposure at Paris, which it is expected will reach down to stars of about the fourteenth magnitude. As each plate is to be limited to four square degrees, and as each star, to avoid possible errors, is to appear on two plates, over 22,000 photographs will be required. For the more accurate determination of the positions of the stars, a *réseau* with lines at distances of 5 m.m. apart is to be previously impressed by a faint line upon the plate, so that the image of the *réseau* will appear together with the images of the stars when the plate is developed. This great work will be divided, according to their latitudes, among eighteen observatories provided with similar instruments, though not necessarily constructed by the same maker. Those in the British dominions and at Tacubaya have been constructed by Sir Howard Grubb.

Besides the plates to form the great chart, a second set of plates for a catalogue is to be taken, with a shorter exposure, which will give stars to the eleventh magnitude only. These plates, by a recent decision of the Permanent Committee, are to be pushed on as actively as possible, though, as far as may be practicable, plates for the chart are to be taken concurrently. Photographing the plates for the catalogue is but the first step in this work, and only supplies the data for the elaborate measurements which have to be made, which are, however, less laborious than would be required for a similar catalogue without the aid of photography.

Already Dr. Gill has nearly brought to conclusion, with the assistance of Professor Kapteyn, a preliminary photographic survey of the Southern heavens.

With an exposure sufficiently long for the faintest stars to impress themselves upon the plate, the accumulating action still goes on for the brighter stars, producing a great enlargement of their images from optical and photographic causes. The question has occupied the attention of many astronomers, whether it is possible to find a law connecting the diameters of these more or less over-

exposed images with the relative brightness of the stars themselves. The answer will come out undoubtedly in the affirmative, though at present the empirical formulae which have been suggested for this purpose differ from each other. Captain Abney proposes to measure the total photographic action, including density as well as size, by the obstruction which the stellar image offers to light.

A further question follows as to the relation which the photographic magnitudes of stars bear to those determined by eye. Visual magnitudes are the physiological expression of the eye's integration of that part of the star's light which extends from the red to the blue. Photographic magnitudes represent the plate's integration of another part of the star's light, namely, from a little below where the power of the eye leaves off in the blue, to where the light is cut off by the glass, or is greatly reduced by want of proper corrections when a refracting telescope is used. It is obvious that the two records are taken by different methods in dissimilar units of different parts of the star's light. In the case of certain coloured stars the photographic brightness is very different from the visual brightness; but in all star changes, especially of a temporary character, may occur in the photographic or the visual region, unaccompanied by a similar change in the other part of the spectrum. For these reasons it would seem desirable that the two sets of magnitudes should be tabulated independently, and be regarded as supplementary of each other.

The determination of the distances of the fixed stars from the small apparent shift of their positions when viewed from widely separated positions of the earth in its orbit, is one of the most refined operations of the observatory. The great precision with which this minute angular quantity, a fraction of a second only, has to be measured, is so delicate an operation with the ordinary micrometer, though, indeed, it was with this instrument that the classical observations of Sir Robert Ball were made, that a special instrument, in which the measures are made by moving the two halves of a divided object-glass, known as a heliometer, has been pressed into this service, and quite recently, in the skilful hands of Dr. Gill and Dr. Elkin, has largely increased our knowledge in this direction.

It is obvious that photography might be here of great service, if we could rely upon measurements of photographs of the same stars taken at suitable intervals of time. Professor Pritchard, to whom is due the honour of having opened this new path, aided by his assistants, has proved by elaborate investigations that measures for parallax may be safely made upon photographic plates, with, of course, the advantages of leisure and repetition; and he has already by this method determined the parallax for twenty-one stars with an accuracy not inferior to that of values previously obtained by purely astronomical methods.

The remarkable successes of astronomical photography, which depend upon the plate's power of accumulation of a very feeble light acting continuously through an exposure of several hours, are worthy to be regarded as a new revelation. The first chapter opened when, in 1880, Dr. Henry Draper obtained a picture of the nebula of Orion; but a more important advance was made in 1883, when Dr. Common, by his photographs, brought to our knowledge details and extensions of this nebula hitherto unknown. A further disclosure took place in 1885, when the Brothers Henry showed for the first time in great detail the spiral nebula issuing from the bright star Maia of the Pleiades, and shortly afterwards nebulous streams about the other stars of this group. In 1886 Mr. Roberts, by means of a photograph to which three hours' exposure had been given, showed the whole background of this group to be nebulous. In the following year Mr. Roberts more than doubled for us the great extension of the nebular region which surrounds the trapezium in the constellation of Orion. By his photographs of the great

nebula in Andromeda, he has shown the true significance of the dark canals which had been seen by the eye. They are in reality spaces between successive rings of bright matter, which appeared nearly straight owing to the inclination in which they lie relatively to us. These bright rings surround an undefined central luminous mass. I have already spoken of this photograph.

Some recent photographs by Mr. Russell show that the great rift in the Milky Way in Argus, which to the eye is void of stars, is in reality uniformly covered with them. Also quite recently Mr. George Hale has photographed the prominences by means of a grating, making use of the lines H and K.

The heavens are richly but very irregularly inwrought with stars. The brighter stars cluster into well-known groups upon a background formed of an enlacement of streams and convoluted windings and intertwined spirals of fainter stars, which becomes richer and more intricate in the irregularly rifted zone of the Milky Way.

We, who form part of the emblazonry, can only see the design distorted and confused; here crowded, there scattered, at another place superposed. The groupings due to our position are mixed up with those which are real.

Can we suppose that each luminous point has no relation to the others near it than the accidental neighbourhood of grains of sand upon the shore, or of particles of the wind-blown dust of the desert? Surely every star from Sirius and Vega down to each grain of the light-dust of the Milky Way has its present place in the heavenly pattern from the slow evolving of its past. We see a system of systems, for the broad features of clusters and streams and spiral windings which mark the general design are reproduced in every part. The whole is in motion, each point shifting its position by miles every second, though from the august magnitude of their distances from us and from each other, it is only by the accumulated movements of years or of generations that some small changes of relative position reveal themselves.

The deciphering of this wonderfully intricate constitution of the heavens will be undoubtedly one of the chief astronomical works of the coming century. The primary task of the sun's motion in space together with the motions of the brighter stars has been already put well within our reach by the spectroscopic method of the measurement of star-motions in the line of sight.

From other directions information is accumulating: from photographs of clusters and parts of the Milky Way, by Roberts in this country, Barnard at the Lick Observatory, and Russell at Sydney; from the counting of stars, and the detection of their configurations, by Holden and by Backhouse; from the mapping of the Milky Way by eye, at Parsonstown; from photographs of the spectra of stars, by Pickering at Harvard and in Peru; and from the exact portraiture of the heavens in the great international star chart which begins this year.

I have but touched some only of the problems of the newer side of astronomy. There are many others which would claim our attention if time permitted. The researches of the Earl of Rosse on lunar radiation, and the work on the same subject and on the sun, by Langley. Observations of lunar heat with an instrument of his own invention by Mr. Boys; and observations of the variation of the moon's heat with its phase by Mr. Frank Very. The discovery of the ultra-violet part of the hydrogen spectrum, not in the laboratory, but from the stars. The confirmation of this spectrum by terrestrial hydrogen in part by H. W. Vogel, and in its all but complete form by Cornu, who found similar series in the ultra-violet spectra of aluminium and thallium. The discovery of a simple formula for the hydrogen series by Balmer. The important question as to the numerical spectral relationship of different substances, especially in connection with their chemical properties; and the further question as to the

origin of the harmonic and other relations between the lines and the groupings of lines of spectra; on these points contributions during the past year have been made by Rudolf v. Kövesligethy, Ames, Hartley, Deslandres, Rydberg, Grünwald, Kayser and Runge, Johnstone Stoney, and others. The remarkable employment of interference phenomena by Professor Michelson for the determination of the size, and distribution of light within them, of the images of objects which when viewed in a telescope subtend an angle less than that subtended by the light-wave at a distance equal to the diameter of the objective. A method applicable not alone to celestial objects, but also to spectral lines, and other questions of molecular physics.

Along the older lines there has not been less activity; by newer methods, by the aid of larger or more accurately constructed instruments, by greater refinement of analysis, knowledge has been increased, especially in precision and minute exactness.

Astronomy, the oldest of the sciences, has more than renewed her youth. At no time in the past has she been so bright with unbounded aspirations and hopes. Never were her temples so numerous, nor the crowd of her votaries so great. The British Astronomical Association formed within the year numbers already about 600 members. Happy is the lot of those who are still on the eastern side of life's meridian!

Already, alas! the original founders of the newer methods are falling out—Kirchhoff, Ångström, D'Arrest, Secchi, Draper, Becquerel; but their places are more than filled; the pace of the race is gaining, but the goal is not and never will be in sight.

Since the time of Newton our knowledge of the phenomena of Nature has wonderfully increased, but man asks, perhaps more earnestly now than in his days, what is the ultimate reality behind the reality of the perceptions? Are they only the pebbles of the beach with which we have been playing? Does not the ocean of ultimate reality and truth lie beyond?

CONTRIBUTIONS TO THE CHEMISTRY OF ERBIUM AND DIDYMIUM.*

By GERHARD KRÜSS.

(Continued from p. 76).

THIS value is not remote from the atomic weight of yttrium, and it is natural that yttria, as a powerful base, should follow didymia. The value found, rather higher than $Y=90$, will have been produced by a slight admixture of terbia, since the oxide obtained by the ignition of the oxalates was yellowish, and not white, like yttria. It is also more probable that terbia, the more powerful base, should follow didymia on fractionation with ammonia than the feebly basic ytterbia.

The double sulphates precipitated by potassium sulphate were converted into nitrate, and the treatment of the didymium with a very large excess of potassium sulphate was again repeated, when only very small quantities of yttria were obtained. The yttria had therefore been almost entirely removed from the didymia by the former treatment.

Whilst potassium-didymium sulphate is very sparingly soluble, the potassium-yttrium sulphate dissolves in 7–8 parts of a slightly acid solution of potassium sulphate.

In order to remove from the didymium any lanthanum possibly present, the precipitated double sulphates were dissolved in much water, precipitated with ammonia, and dissolved in sulphuric acid after washing the potassium salt out of the precipitate. The sulphate obtained was

* *Liebig's Annalen.*

evaporated, converted into the anhydrous salt, and added to ice-water in small portions with constant stirring. The sulphate dissolved slowly but completely, and was heated to 40° according to Mosander's method, and afterwards to a higher temperature. No separation of lanthanum sulphate took place, and the sulphate which remained in solution was again converted into nitrate. In this manner there was obtained from gadolinite a pure preparation of didymium. It contained mere traces of samarium; scandium could scarcely be present at the outset, as the crude earths had been most carefully fractionated with ammonia, and scandium would be more likely to accompany erbium than didymium.

The requisites were—

1. A relatively short series of fractional precipitations with ammonia, from a very dilute solution (removal of cerium, ytterbium, scandium, erbium).
2. Treatment with chlorine in an alkaline liquid (removal of the last traces of cerium).
3. Twice crystallisation with an excess of potassium sulphate (removal of yttrium and terbium).
4. Heating the solution of anhydrous sulphate in ice-water to 40° (removal of lanthanum).

Instead of often repeating this last method in case of a large quantity of lanthanum, it is better to precipitate fractionally with ammonia, as proposed by Cleve, when lanthanum behaves as the more powerful base.

The didymium obtained had a mean atomic weight of $R = 145$, and its preparation was relatively convenient. Erbium material could also be obtained from the above mentioned more feebly basic ammonia fractions of the earths gadolinite, without a fractionated decomposition of the nitrates by heat.

Fractionation of Erbium Material by Aniline in an Alcoholic Solution.

Erbia can be naturally more easily separated by fractionated precipitation from the stronger bases of the rare earths, such as didymia, than from the other weak bases, the oxides of holmium, thulium, and ytterbium. An approximate separation of these earths,—at least, as far as the preparation of pure ytterbium is concerned—may certainly be effected by resolving the mixed earthy nitrates by cautious fusion partially into basic salts insoluble in water, and repeating this fractionation systematically about 500 times. (See Nilson's "Researches on Ytterbium and Scandium," *Berichte Deutsch. Chem. Gesell.*, xiii., 1430, 1439; xii., 550, 554).

It was not practicable to separate quickly the feebly basic rare earths from each other by fractionated precipitation with ammonia. The author further tried whether a method for separating erbium from holmium, thulium, and ytterbium might be found upon Lecoq de Boisbaudran's observation (*Comptes Rendus*, cxi., 394), that the rare earths in presence of ammonium acetate are slowly and only partially precipitable by an excess of ammonia. The results were negative.

The following experiments were successful:—

On fractionating the earths with ammonia all the weak bases were accumulated in the fractions rich in erbium. The rare earths which accompany erbia, and erbia itself, under the experimental conditions above described, had behaved as bases weaker than ammonia diluted as above. A weaker base than dilute ammonia had therefore to be used if a precipitant was sought for separating, e.g., erbia from ytterbia. It must be more strongly basic than ytterbia, but weaker than erbia, and consequently it must either not precipitate erbia at all from its solutions, or but very imperfectly.

Attempts were made to precipitate alcoholic solutions of neutral earthy salts, with alcoholic solutions of substituted ammonias. For this purpose the chlorides of the rare earths were used, the solutions being purified as far as possible from free hydrochloric acid by repeated evaporation upon the water-bath. The purpose of this elimi-

nation of acid was to prevent the excess of hydrochloric acid from forming at once with aniline a hydrochlorate, which, if present in considerable quantities, greatly interferes with the precipitation even of the weakest bases among the rare earths by aniline.

The chlorides were taken up in alcohol at 50 per cent, and the organic bases were also dissolved in alcohol of the same strength.

If an earthy chloride which contains all the earths of gadolinite is first mixed with more aniline than is calculated according to the mean equivalent weight of the oxides, on the supposition that all oxide is precipitated, it appears, in fact, that the solution of chloride is only partially precipitated as hydroxide. If the solution containing an excess of aniline is filtered off and heated for some time to about 80°, there occurs a new precipitation of hydroxide, and even still a part of the earthy chloride is not decomposed by the excess of aniline present.

Aniline has thus behaved as a base feebler than a part of the rare earths. At the same time it is perceived that the aniline precipitations at the temperature of the room possess a fainter absorption spectrum than the precipitations at higher temperatures, the conditions being otherwise equal. At lower temperatures relatively more colourless earths are precipitated, and as these were first separated out of the mixture they were the weakest earths, especially therefore ytterbia.

Consequently aniline seemed suitable to eliminate the weakest bases from a material rich in erbia. In order to bring into more prominence the different behaviour of aniline in heat and cold, alcoholic solutions of chlorides of erbium material were mixed at 0° with an excess of alcoholic solutions of aniline. No precipitation took place, whence they were gradually heated by standing in the room until precipitation began. The liquid was then filtered, and the atomic weights of the earthy metals in the solution and the precipitate were determined.

Experiment 1.—A solution of chloride, containing chiefly erbium and ytterbium and some yttrium, was resolved under the conditions given into an aniline precipitate and a filtrate. The earthy mixture used in the

experiment when converted from oxide into sulphate R had the weight = 161.81. The determination of the equivalents of the oxides present in the filtrate, and in the aniline precipitate, gave for the precipitate

$R = 168.75$, and for the filtrate $R = 158.38$.

Experiment 2 was conducted under the same conditions with a material which contained in addition to erbium and ytterbium relatively much yttrium.

	Atom Weight.
R in the earth employed.. .. .	= 131.07
" " oxide of the aniline precipitate ..	= 151.13
" " " filtrate.. .. .	= 128.92

The precipitation of the earthy hydroxides with an alcoholic solution of aniline in the cold is an easy and neat operation, and if executed *only once* resolves an erbium material containing oxides of closely approximating basicity to a very considerable degree, as the above figures show.

Hence, large quantities of materials rich in erbium should be systematically worked up by precipitation with aniline, and the behaviour of "old" erbium should be tested by fractionated treatment with other ammonia bases.

Behaviour of the Earths with Ammonium Carbonate.

We learn from the researches of Berzelius, H. Rose, Marignac, Höglund, Stapf, that salts of lanthanum, yttrium, erbium, glucinum, thorium, and zirconium are precipitated by ammonium carbonate, and that the precipitated basic carbonates are re-dissolved in part readily and in part gradually in an excess of ammonium carbonate. Basic didymium carbonate, however, according to

Marignac, is almost insoluble in an excess of ammonium carbonate.

A neutral nitric solution of mixed earths of gadolinite was poured, whilst stirring, into a concentrated solution of ammonium carbonate (10 parts carbonate to 1 part of earth), and the precipitate was digested for 24 hours in the supernatant liquid. After the precipitate had been washed upon the filter with a solution of ammonium carbonate it was converted into nitrate. In its spectrum didymium lines were almost exclusively visible, and the erbium lines had nearly disappeared. If the material was rich in erbium the digestion with carbonate must be frequently repeated.

A current of steam is then passed through the mixed filtrates for some hours, when the ammonium carbonate is decomposed and a basic carbonate is deposited. This was filtered and converted into neutral nitrate. In its spectrum few didymium lines are present, but almost exclusively erbium and X lines. According to its spectrum the erbium, after being once digested, is almost as pure as if it had been obtained from a mixture of erbium and didymium by a twice repeated treatment of the mixed saline solution with potassium sulphate.

It must be remarked that erbium carbonate is but slightly soluble in ammonium carbonate, especially when, as in the case before us, it has been precipitated as a basic carbonate along with didymium. Thus, in the above experiment, from about 400 grms. of mixed earths, certainly poor in erbia, there were obtained only 5 grms. of erbia by a single digestion with ammonium carbonate. The above method is not adapted for obtaining large quantities of erbia from a mixture of the earths which yield absorption spectra; for this purpose fractionation with ammonia is preferable. But it is advantageous to digest didymium containing only small quantities of erbium with an excess of ammonium carbonate.

(To be continued.)

NOTICES OF BOOKS.

The International Annual of Anthony's Photographic Bulletin. New York: E. and H. T. Anthony and Co. London: Iliffe and Son.

THIS publication, now in its fourth year, consists of a selection of essays relative to the practical or to the theoretical phase of photography. These chapters are necessarily of a very promiscuous character. A humorous essay "To Correspondents" touches on the difficulties of an editor required by his readers to be omniscient. Says the writer:—"Time was when questions anent the sciences, the fine arts, and the industrial arts, were propounded by those in search of useful knowledge in various technical journals; but with the advent of the 'press the button' system we have reached the present stage in the process of levelling, and Susan Jane can study in the pages of her especial organ, the *Family Journal*, how to remove superfluous hair from the female face, how to repel the advances of a too forward milkman, and what is the best developer for dry plates, which, no matter how long a time or how short a time they are exposed, never have any picture upon them when finished."

On the applications of photography in scientific research we find but little. Still there is, we think, evidence here, as elsewhere, that photographers are now less exclusively given to taking portraits than was the case in the infancy of the art. The conflict between the amateur and the professional, and, again, the controversy between photography and "high art," are still raging.

One of the writers mentions, incidentally, that the present rage for photography has superseded the microscopy-fever of the last decennium. The selfsame hands that then manipulated the microscope and its accessories

now wield the camera. Unfortunately a majority do as little good with one instrument as with the other.

The Chemical Analysis of Iron. A Complete Account of all the best known Methods for the Analysis of Iron, Steel, Pig-iron, Iron-ore, Limestone, Slag, Clay, Sand, Coal, Coke, and Furnace and Produce Gases. By ANDREW ALEXANDER BLAIR. Second Edition, 8vo., pp. 314. Philadelphia: J. B. Lippincott and Co.

WE are not surprised that a second edition of this useful and trustworthy work has been already called for. In general arrangement the present edition differs little from its forerunner, but a variety of modifications have been introduced in accordance with recent improvements in chemical analysis.

The get-up of the book has a much more ornamental character than we usually find among scientific publications. The illustrations are beautifully clear. Marginal notes furnish a running key to the subject-matter of the text, and will save the reader much trouble. At the same time footnotes give the authors of the various methods. The paper is of that glazed or calendered quality which has now become so fashionable, but which we think is not to be recommended, as the light which it reflects is fatiguing to the eyes.

CORRESPONDENCE.

THE INSTITUTE AND THE ALIEN.

To the Editor of the Chemical News.

SIR,—A great scandal has come to light among public analysts. The provisions of the Alien Act render aliens ineligible for the office of public analyst. The Local Government Board, which has to confirm each appointment of a public analyst before he can enter upon the discharge of the duties of his office, would not knowingly sanction the appointment of aliens, and yet, notwithstanding the Act and the Board, it is undeniable that for years several of these appointments have been in alien hands. The matter is grave,—far graver than would appear at first sight.

There is no doubt whatever of the state of the law in this respect, and the alien public analyst is no public analyst at all, but a mere counterfeit of the duly qualified public officer. Every tradesman who has been convicted and punished, in cases where the services of the alien public analyst have been required, is entitled to demand the quashing of the proceedings in his case on the score of flagrant irregularity.

The existence of such a being as the alien public analyst was made out a short time ago by my friend Mr. Johnstone, who took the bold step of writing to the authorities in districts where the public analyst was an alien, and offering himself as a candidate for the vacant office. The alien who has been usurping the office of public analyst for many years, and has thereby created a great scandal, complained to the Institute of Chemistry, which forthwith expelled Mr. Johnstone, who has performed a signal public service, they mistaking that performance for unprofessional conduct.—I am, &c.,

J. ALFRED WANKLYN.

MISCELLANEOUS.

Honours for Scientific Men.—*A propos* of the fact that Dr. Hyde Mijake, Professor in the Medical Faculty of the University of Tokio, has been nominated a member of the Japanese House of Peers, a medical contem-

porary complains that "in our highly favoured country" medical men, however eminent, can rise no higher than to a baronetcy. With scientific men in general the case is the same. We have had among us a family, two members of which—father and son—achieved a world wide and an enduring reputation for scientific researches. A baronetcy was awarded to them; but the grandson, throwing himself into law and politics, has gained a peerage, though his celebrity is small indeed compared to that of his father and grandfather. Leaving law and finance out of the question, even literature has scored four peerages within the lifetime of the present generation,—Science none! Would not a large proportion of our best minds be attracted to Science if it was not, in the distribution of honours, so entirely left out in the cold?

New Decree concerning Methylated Spirit.—In addition to the 10 per cent of (impure) methyl alcohol with which alcohol has to be spoiled, in this country, before it can be sold duty-free for industrial purposes, the Board of Inland Revenue now demand that there shall be further added, in every 100 gallons, 12 gills of mineral naphtha of the specific gravity of not less than 0.800. We fear that this addition will interfere with some of the technical uses of this spirit. Why do not the advisers of the Inland Revenue recommend the addition of a trace of Dippel's animal oil, which renders the mixture absolutely undrinkable, whilst, from the minuteness of the dose required, it does not perplex the manufacturer?

Gautter's Method for the Determination of Tannin.—MM. Schroeder and Passler.—The authors criticise Gautter's method, which they consider one of the best of the known processes. It has an advantage over that of Löwenthal, as it can be carried out without extensive previous experience and gives concordant results. On the other hand, Löwenthal's method has the advantage that substances other than tannin, such as hydrocarbons and organic acids, are not acted upon. Gautter's method is not applicable for determining the tannin in dye liquors. The authors operate as follows:—The liquid to be titrated is placed in a flask holding 350 c.c., and heated to a gentle boil after the addition of 0.5 c.c. dilute sulphuric acid (1:5) to 1 m.grm. of the dry tannin substance. The flask is then removed from the fire, the solution of permanganate is let flow in by 1 c.c. at a time, shaking for five seconds after each addition. The red colour disappears more and more slowly, and ultimately remains after shaking for five seconds. The contents of the flask are then again heated to boiling, permanganate is again run in by c.c.'s, keeping the liquid boiling for one minute after each addition. This addition is continued until there is formed a copious precipitate of manganese hydroxide, which scarcely decreases after boiling for a minute. The number of c.c. consumed is noted, and the titration is considered satisfactory only if the solution consumed comes to 1—2 c.c. more than the final result shows. After the appearance of the strong permanent precipitate 5 c.c. permanganate are further added without heating; oxalic acid is then added until the solution becomes perfectly clear, and it is then titrated to completion with permanganate. At the end of the titration they take the point when the red colour remains for half a minute. For standardising the authors use a solution of tannin containing about 2 grms. dry substance per litre, using from 10—25 c.c. of this solution for titration. In disputed cases the gravimetric method must be regarded as decisive.—*Zeit. fur Anal. Chemie*, xxix., Part 6.

Purification of Sulphuretted Hydrogen for Criminal Investigations.—Oscar Jacobson (*Berichte*).—Arsenic hydride and iodine decompose each other to arsenic iodide and hydriodic acid, whilst hydrogen sulphide has no action upon iodine, either solid or dissolved, in strong hydriodic acid. Sulphuretted hydrogen can be obtained absolutely free from arsenic if passed over solid iodine.—*Zeit. fur Anal. Chemie*, xxix., Part 6.

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ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

By Professor W. C. ROBERTS-AUSTEN, C.B., F.R.S.,
President of the Section.

CARDIFF, 1891.

THE selection of Cardiff as a place of meeting of the British Association led to the presidency of Section B being entrusted to a metallurgist. It will be well, therefore, to deal in this address mainly with considerations connected with the subject to which my life has been devoted, and I hope that it may be possible for me to show that this practical art has both promoted the advancement of science and has received splendid gifts in return.

It is an art for which in this country we have traditional love; nevertheless the mode of teaching it, and its influence on science, are but imperfectly understood and appreciated. Practical metallurgists are far too apt to think that improvements in their processes are mainly the result of their own experience and observation, unaided by pure science. On the other hand, those who teach metallurgy often forget that for the present they have not only to give instruction in the method of conducting technical operations, but have truly to educate, by teaching the chemistry of high temperatures, at which ordinary reactions are modified or even reversed, while they have further to deal with many phenomena of much importance, which cannot, as yet, be traced to the action of elements in fixed atomic proportions, or in which the direct influence of the atom is only beginning to be recognised.

The development of a particular art, like that of an organism, proceeds from its internal activity; it is work which promotes its growth and not the external influence of the environment. In the early stage of the development of an industry the craftsmen gather a store of facts which afford a basis for the labours of the investigator, who penetrates the circle of the "mystery" and renders knowledge scientific. Browning, inspired by the labours of a chemist, finely tells us in his "Paracelsus":—

To know
Rather consists in opening out a way
Whence the imprisoned splendor may escape,
Than in effecting entry for a light
Supposed to be without.

If it be asked who did most in gaining the industrial treasure and in revealing the light of chemical knowledge, the answer is certainly the metallurgists whose labours in this respect differ materially from others which have ministered to the welfare of mankind. First it may be urged that in no other art have the relations between theory and practice been so close and enduring. Bacon, who never undervalued research, tells us that in the division of the labour of investigation in the New Atlantis there are some "that raise the former discoveries by experiment into greater observations, axioms, and aphorisms: these we call the *interpreters of nature*." There are also others "that bend themselves, looking into the experiments of their fellows and casting about how to draw out of them things of use and practice for man's life and knowledge . . . these we call the *dowry men or benefactors*." In reviewing the history of metallurgy, especially in our islands, it would seem that the two classes of workers, the interpreters of nature and the practical men, have for centuries sat in joint committee,

and, by bringing theoretical speculation into close connection with hard industrial facts, have "carried us nearer the essence of truth."

The main theme of this address will therefore be the relation between theory and practice in metallurgy, with special reference to the indebtedness of the practical man to the scientific investigator.

We will then consider—

- (1). Certain facts connected with "Oxidation" and "Reduction," upon which depend operations of special importance to the metallurgist.
- (2). The influence in metallurgical practice of reactions which are either limited or reversible.
- (3). The means by which progress in the metallurgical art may be effected, and the special need for studying the molecular constitution of metals and alloys.

(1). The present year is a memorable one for chemists, being the centenary of the birth of Faraday and the bi-centenary of the death of Robert Boyle. The work of the former has recently been lovingly and fittingly dealt with in the Royal Institution, where he laboured so long. I would, in turn, briefly recal the services of Boyle, not, however, on account of the coincidence of date, but because with him a new era in chemistry began. He knew too much about the marvellous action of "traces" of elements on masses of metal to feel justified in pronouncing absolutely against the possibilities of transmutation, but he did splendid service by sweeping away the firm belief that metals consist of sulphur, salt, and mercury, and by giving us the definition of an element. He recognised the preponderating influence of metallurgy in the early history of science, and quaintly tells us that "those addicted to chemistry have scarce any views but to the preparation of medicines or to the improvement of metals," a statement which was perfectly correct, for chemistry was built up on a therapeutic as well as a metallurgical basis. The fact is, however, that neither the preparation of materials to be employed in healing, nor the study of their action, had anything like the influence on the growth of theoretical chemistry which was exerted by a few simple metallurgical processes. Again, strange as it may seem, theoretical chemistry was more directly advanced by observations made in connection with methods of purifying the precious metals, and by the recognition of the quantitative significance of the results, than by the acquisition of facts incidentally gathered in the search for a transmuting agent. The belief that chemistry "grew out of alchemy" nevertheless prevails, and has found expression in this Section of the British Association. As a fact, however, the great metallurgists treated the search for a transmuting agent with contempt, and taught the necessity of investigation for its own sake. George Agricola, the most distinguished of the sixteenth-century metallurgists, in his work "*De Ortu et Causis Subterraneorum*" (lib. v.), written about the year 1539, disdainfully rejects both the view of the alchemists that metals consist of sulphur and mercury, and their pretended ability to change silver into gold by the addition of foreign matter.

Biringuccio (1540) says:—"I am one of those who ignore the art of the alchemists entirely. They mock nature when they say that with their medicines they correct its defects, and render imperfect metals perfect." "The art," he adds, "was not worthy of the consideration of the wise ancients who strove to obtain possible things." In his time, reaction between elements meant their destruction and re-constitution, nevertheless his sentence "transmutation is impossible, because in order to transmute a body you must begin by destroying it altogether," suggests that he realised the great principle of the conservation of mass upon which the science of chemistry is based. We have also the testimony of the German metallurgist, Becher, who improved our tin-smelting in Cornwall. He is said to have caused a medal

to be struck in 1675, which bore the legend: "Hanc unciam argenti finissimi ex plumbo arte alchymica transmutavi," though he should have been aware that he had only extracted the precious metal from the lead, and had not transmuted the base one. This is a lapse which must be forgiven him, for his *terra pinguis* was the basis of the theory of Phlogiston, which exerted so profound an influence for a century after his death, and he wrote:—"I wist that I have got hold of my pitcher by the right handle, for the pseudo-chemists seek gold, but I have the true philosophy, science, which is more precious."

At this critical period what was Boyle doing when the theory of Phlogiston dawned in the mind of the metallurgist Becher? In 1672 Boyle wrote his paper on "Fire and Flame Weighed in the Balance," and came to the conclusion that the "ponderous parts of flame" could pass through glass to get at melted lead contained in a closed vessel. It has been considered strange that he did not interpret the experiment correctly, but he, like the phlogistic chemists, tried to show that the *subtilis ignis*, the material of fire or phlogiston, would penetrate all things, and could be gained or lost by them. Moreover, his later experiments showed him that glass was powerless to screen iron from the "effluvium of a loadstone." His experiment with lead heated in a closed glass vessel was a fundamental one, to which his mind would naturally revert if he could come back now and review the present state of our knowledge in the light of the investigations which have been made in the two centuries that have passed since his own work ceased. If he turned to the end of the first century after his death, he would see that the failure to appreciate the work of predecessors was as prevalent in the eighteenth century as in the sixteenth. The spirit of intolerance which led Paracelsus to publicly burn, in his inaugural lecture at Basle, the works of Galen, Hippocrates, and Avicenna, survived in the eighteenth century when Madame Lavoisier burnt the works of Stahl, but it was reserved for the nineteenth century to reverently gather the ashes, recognising that when the writers of the School of Becher spoke of Phlogiston they meant what we understand by potential energy.

If Boyle, finding that the Fellows of the Royal Society had not carried out their intention to build a "Repository and Laboratory," sought the School of Mines and came to the Royal College of Science, he would surely thank my colleague, Professor Thorpe, for his vigorous defence last year, as President of this Section, of the originality of the work of Priestley and Cavendish, to which Boyle's own researches had directly led. We, on our part, remembering Berzelius's view that "oxygen is the centre point round which chemistry revolves," would hope to interest him most by selecting the experiments which arose out of the old metallurgical operation of separating the precious metals from lead by "cupellation." When, in conducting this operation, lead is heated in the presence of air it becomes converted into a very fluid dross. Boyle had, in 1661, taken this operation as the very first illustration to his "Sceptical Chemist" in proof of his argument as to the elemental nature of metals. He would remember the quantitative work of Geber in the eighth century, who stated that the lead so heated in air acquired a "new weight," and he would appreciate the constant reference to the operation of cupellation from the close of the sixth century, B.C., when the prophet Jeremiah wrote, to the work of Jean Rey in 1629, whose conclusions he would wish he had examined more closely. Lord Brouncker, as first President of the Royal Society, had called attention to the increase in weight of the lead in the "coppels" in the Assay Office in the Mint in the Tower, and Mayo had shown that the increase in weight comes from a distinct "*spiritus*" in the air. Boyle would incidentally see that Newton had accepted office in the Mint, where he doubtless continued his experiments on calcination begun some time before, and, as if to mark his interest in the operation of assaying, figures are repre-

sented on a bas-relief on his tomb in Westminster Abbey as conducting cupellation in a muffle. The old work merges wonderfully into the new. Chevreul, in the nineteenth century, confirms Otto Tachens' view in the seventeenth, as to the saponifying action of litharge. Deville employs molten litharge to absorb oxygen dissociated from its compounds, and Graham, by extracting occluded gases from iron and other metals, proves the accuracy of the old belief that elastic fluids can freely permeate even solid metals.

We may imagine with what vivid interest Boyle would turn, not merely to the results of Priestley's work, but to his methods. Priestley had decomposed litharge with the electric spark, and had satisfied himself in 1774, by heating red-lead, that the gas he obtained in his earlier experiments was really the one now called oxygen.

Boyle would see that in the period 1774-7 Lavoisier, being attracted by the "sceptical chemist's" own experiment on the heating of lead in closed vessels, overthrew the Phlogistic theory and placed chemistry on a firm basis by showing that the increase in weight of lead and tin, when heated in air, represents exactly the weight of the gaseous body added, and, finally, Dalton having developed the atomic theory and applied it to chemistry, Berzelius made lead memorable by selecting it for the first determination of an atomic weight.

Without diverting his attention from the phenomena of oxidation, Boyle would find questions the interest of which is only equalled by their present obscurity. He would contemplate the most interesting phase of the history of chemical science, described by Van 't Hoff as that of its evolution from the descriptive to the rational period, in the early days of which the impossibility of separating physics and chemistry became evident, and Boyle would find that chemistry is now regarded from the point of view of the mechanics of the atoms.

Deville's experiments on dissociation have rendered it possible to extend to the groups of atoms in chemical systems the laws which govern the fusion and vapourisation of masses of matter, and this has produced a revolution comparable in its importance to that which followed the discovery of the law of definite proportions, for dissociation has shown us that true causes of chemical change are variations of pressure and of temperature. For instance, oxygen may be prepared on an industrial scale from air by the intervention of oxide of barium heated to a constant temperature of 700° provided air be admitted to the heated oxide of barium, under a pressure of 1½ atmospheres, while the oxygen thus absorbed is evolved if the containing vessel be rendered partially vacuum. It will be evident, therefore, that at a certain critical temperature and pressure the slightest variation of either will destroy the equilibrium of the system and induce chemical change.

The aim of Boyle's chemical writings was to show that no barrier exists between physics and chemistry, and to "serve the commonwealth of learning by begetting a good understanding betwixt the chemists and the mechanical philosophers," who had, as he said, "been too great strangers to each other's discoveries." In view of the dominant lines of research which occupy chemists at the present time, such, for instance, as the investigations of "Osmotic pressure" and of the application of Boyle's own law to salts in solution, he would feel that his hope had been realised, and that, though he lived a century too soon to take part in Berthollet's discussion with Proust, he nevertheless shares Berthollet's triumph in the long-delayed but now rapid development of chemistry as a branch of applied mechanics.

We need, however, no longer look at these questions from the point of view of Boyle, for our own interest in the application of chemical mechanics to metallurgy is sufficiently vivid, as instances to be given subsequently will show.

Hitherto I have mainly dwelt on questions relating to oxidation, but not less interesting is the history of the

steps by which an accurate knowledge was acquired of the other great process practised by the metallurgist, the one to which Paracelsus was the first to apply the name of "Reduction." Its explanation followed naturally from the elucidation of the phenomena of combustion by Lavoisier, who, in continuation of Macquer's experiments of 1771, proved, in conjunction with other workers, that carbonic anhydride is produced when the diamond is burnt in air or oxygen. Carbon has been known for ages as the most important of the reducing agents, but when, in 1772, Lavoisier heated oxide of lead and carbon together, he did not at first recognise that carbonic anhydride had been produced, simply because the volume of the gas set free was the same as if oxygen merely had been liberated. He soon, however, saw that neither the carbon alone, nor the oxide of lead alone, gave rise to the evolution of carbonic anhydride, which resulted from the *mutual action* of carbon and a constituent of the litharge. "This last observation leads us insensibly," he adds, "to very important reflections on the use of carbon in the reduction of metals." It most certainly did, and by 1815 an accurate, if incomplete, view of reduction had passed into the encyclopædias. It was seen that the removal of oxygen from burnt metals by carbon, "give the metals," as Fourcroy and Vauquelin put it, "a new existence." Some ten years later Le Play attempted to show that reduction is always effected by the intervention of carbonic oxide, which elicited the classical rejoinder from Gay-Lussac, who pointed out that "carbon alone, and at very moderate temperatures, will reduce certain metallic oxides without the intervention of carbonic oxide or of any other elastic fluid." I mention these facts because metallurgists are slow to recognise their indebtedness to investigators, and too often ignore the extreme pains with which an accurate knowledge has been acquired of the principles upon which their processes have been based.

The importance of a coherent explanation of reduction in smelting pig-iron is enormous. The largest blast-furnaces in 1815 hardly exceeded those in use in the previous century, and were at most only 40 feet high with a capacity of 5000 cubic feet. At the present day their gigantic successors are sometimes 90 feet high with a capacity of 25,000 cubic feet. This development of the blast-furnace is due to the researches of a number of investigators, among whom Von Tunner, Lowthian Bell, and Gruner deserve special mention. We are, however, forcibly reminded of the present incompleteness of our knowledge of the mechanism of reduction, when we remember that the experiments of H. P. Baker have led us to believe that pure carbon cannot be burnt in perfectly dry and pure oxygen, and therefore that the reducing agent, carbonic oxide, cannot be produced at all unless moisture be present.

Ludwig Mond, Langer, and Quincke, teach us not only that nickel can separate carbon from carbonic oxide, but the wholly unexpected fact that dry carbonic oxide can at a temperature of 100° take up nickel, which it again deposits if heated to 150°. Mond and Quincke, and independently Berthelot, have since proved the existence of the corresponding compound of iron and carbonic oxide, and it may safely be concluded that in the blast-furnace smelting iron this peculiar action of carbonic oxide plays an important part, and it doubtless aids the carburisation of iron by cementation. It is truly remarkable that the past year should have brought us so great an increase in our knowledge of what takes place in the reduction of an oxide of iron, and in the carburisation of the liberated metal. My own experiments have, I trust, made it clear that iron can, at an elevated temperature, be carburised by the diamond *in vacuo*; that is, in the absence of anything more than "a trace" of an elastic fluid or of any third element. Osmond has further shown, within the last few months, that the action between iron and carbon is a mutual one; for though carbon in the pure diamond form carburises iron, the metal in its turn, at a temper-

ature of 1050°, attacks the diamond, invests it with a black layer, and truly unites with it.

The question of the direct carburisation of iron (Darby's process) by filtering the molten metal through carbon, promises to be of much importance, for at present, as is well known, two millions of tons of steel which are made in the Bessemer converter in this country alone, are re-carburised after "the blow" by the addition of spiegeleisen.

Carbonic oxide, moreover, would appear to be more chemically active than had been supposed; for during the present year Berthelot has shown that the perfectly pure gas heated to 500° or 550° produces carbonic anhydride with deposition of carbon at red heat, not by ordinary dissociation, but by decomposition preceded by polymerisation. He further shows that carbonic oxide will decompose ammoniacal nitrate of silver, and thus brings it into close connection with the aldehyds.

(2.) In turning to the modern aspects of metallurgical practice, we shall see that the whole range of the metallurgist's field of study is changing. It is no longer possible for him to devise a series of operations on the evidence afforded by a set of equations which indicate the completion of an operation; he has, as I have already suggested, to consider the complicated problems which have been introduced into chemistry from the sciences of physics and mechanics. He has, in fact, no longer to deal merely with atoms and molecules, but with the influence of mass. As Ostwald points out, we are reminded that many chemical processes are reciprocating so that the original products may be obtained from the product of the reaction. The result of such opposed processes is a state of CHEMICAL EQUILIBRIUM, in which both the original and the newly-formed substances are present in definite quantities that remain the same so long as the conditions, more especially temperature and pressure, do not undergo further change. Again, in very many metallurgical processes, reactions are rendered incomplete by the limitations imposed by the presence of bodies which cannot be speedily eliminated from the system, and the result may be to greatly retard the completion of an operation. The time has come when the principles of dynamic chemistry must be applied to the study of metallurgical problems if they are to be correctly understood, and it is, moreover, necessary to remember the part played by the surface separating the different aggregates in contact with one another. When, for instance, a reaction has to take place accompanied by the evolution of gas, there must be space into which the gas can pass. The rate, therefore, at which change takes place will obviously depend on the state of division of the mass.

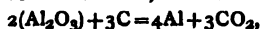
One of the most remarkable points in the whole range of chemistry is the action engendered between two elements capable of reacting by the presence of a third body. It may be, and this is the most wonderful fact of all, that merely a trace of a third body is necessary to induce reaction, or to profoundly modify the structure of a metal. H. Le Chatelier and Mouret have pointed out that in certain cases it is inaccurate to say that the third body causes the reaction to take place, because, after it has destroyed the inter-molecular resistances which prevented the reaction taking place, the third body ceases to intervene. This is apparently the case when platinum sponge effects the union of oxygen and hydrogen, or conversely, when very hot platinum splits up water vapour into its constituent gases. Future investigation will, it is to be hoped, show whether the platinum does not exert some direct action in both cases. We can no longer neglect the study of such questions from the point of view of their practical application. The manufacture of red-lead presents a case in point. In "drossing" molten lead the oxidation of the lead is greatly promoted by the presence of a trace of antimony, and conversely, in the separation of silver from molten lead, by the aid of zinc,

H. Roessler and Endelmann have recently shown that aluminium has a remarkable effect in protecting the zinc from loss by oxidation, and, further, the presence of one-thousandth part of aluminium in the zinc is sufficient to exert this protecting action on that metal. I am satisfied that if our metallurgists are to advance their industrial practice, they must, if I may use such an expression, persistently think in calories, and not merely employ the ordinary atomic "tools of thought." They will then be able to state what reactions can, under given conditions, take place; to indicate those which will be completed; and to avoid those that are impracticable.

In France, the country of so many great metallurgists, men like Le Chatelier and Ditté are doing admirable service, by bringing the results of the labours and teaching of Ste. Claire Deville within the range of practical men. And if I do not refer more specifically to their work it is for want of space and not of appreciation, but a few simple cases of reversible actions will perhaps make the subject clear. In the blast-furnace the main reducing agent, carbonic oxide, is produced from the solid fuel by the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$, a reaction which is theoretically impossible because it is endothermic, and would be attended by absorption of heat. But heat external to the system intervenes, and acts either by depolymerising the carbon into a simpler form which can combine with oxygen of the CO_2 with evolution of heat, or, by dissociating carbonic anhydride, sets oxygen free which combines with the carbon. Reduction of oxide of iron in the blast-furnace is mainly effected by carbonic oxide according to the well-known reaction—



But the gas issuing from a blast-furnace contains carbonic oxide, an important source of heat. The view that this loss of carbonic oxide was due to the fact that the contact of the ore and the reducing gas was not sufficiently prolonged, led to a great increase in the height of blast-furnaces, but without, as Gruner showed, diminishing the proportion of carbonic oxide escaping from the throat. The reduction of an iron ore by carbonic oxide only takes place within certain well-defined limits, and a knowledge of the laws of chemical equilibrium would have saved thousands and thousands of pounds which have been wasted in building unduly high furnaces. I would add that large sums have also been sacrificed in the vain attempt to smelt oxide of zinc in the blast-furnace, for which operation patents have frequently been sought, in ignorance or defiance of the readiness with which the inverse action occurs, so that the reducing action of carbon on oxide of zinc may be balanced by the re-oxidation of the reduced zinc by carbonic anhydride, which is the product of the reduction. A further instance may be borrowed from an electro-chemical process which has been adopted for obtaining alloys of aluminium. As is well known, all attempts to effect the direct reduction of alumina by carbon have failed, because the reaction—



requires 783·2 calories, while only 291 calories would result from the conversion of carbon into carbonic anhydride, therefore the reaction cannot be effected; but in Cowle's process aluminium is nevertheless liberated when alumina is mixed with charcoal and strongly heated by the passage of an electric current. This result is due, not to a simple reduction of alumina, but to its dissociation at the high temperature produced by the passage of a current of 1600 amperes between carbon poles, the liberated aluminium being at once removed from the system by metallic copper which is simultaneously present and may not be without action itself.

An instance of the importance of these considerations is presented in the manufacture of steel by the basic process. Much care is devoted to obtaining conditions which will ensure not only the elimination, but the order of the disappearance of the impurities from the molten pig-iron. In the basic process, as conducted in the closed

converter, the phosphorus does not disappear until the carbon has left the fluid bath, whilst, when the open hearth furnace is used, the elimination of the phosphorus may be effected before that of the carbon, and it is asserted that if the carbon goes before the phosphorus is got rid of, a further addition of carbon is necessary. A curious and subtle case of chemical equilibrium is here presented. In the open hearth furnace and Bessemer converter respectively, the temperatures and pressures are different, and the conditions as to the presentation of oxygen to the fluid bath are not the same. The result is that the relative rates of oxidation of the phosphorus and carbon are different in the two cases, although in either case, with a given method of working, there must be a ratio between the phosphorus and carbon in which they disappear simultaneously. The industrial bearing of the question is very remarkable. In the basic Bessemer process the tendency of the phosphorus to linger in the bath renders an "after-blow" necessary, it may be only of a few seconds' duration, but much iron is nevertheless burnt and wasted, and Mr. Gilchrist tells me that if this after-blow could be avoided, a saving of some 6 per cent of the yield of steel would be effected annually, the value of which, at the present rate of output and price of steel, is no less than a quarter of a million sterling.

The volatilisation of sulphur in the converter while it is retained by the steel in the open-hearth furnace, and the increase in the percentage of manganese, which leaves the slag and returns to the bath of metal in the converter at the end of the "blow," will probably be traced to the disturbance of equilibrium which attends very slight variations in the conditions, especially as regards temperature and pressure, under which the operations are conducted.

In the blast-furnace the reducing action must be greatly dependent on the rate at which alkaline cyanides are formed, and Hempel has recently shown, by the aid of well-devised experiments, that the quantity of cyanides which may be obtained at a high temperature from carbon, nitrogen, and alkaline oxides, increases as the pressure becomes greater.

Metallurgical chemistry is, in fact, a special branch of chemical science which does not come within the ordinary sphere of the academic teaching of chemistry. It is often urged that metallurgical practice depends upon the application of chemical principles which are well taught in every large centre of instruction in this country, but a long series of chemical reactions exist which are of vital importance to the metallurgist, though they are not set forth in any British manual of chemistry, nor are dealt with in courses of purely chemical lectures. I feel bound to insist upon this point, because, as Examiner in Metallurgy for the Science and Art Department, I find that purely analytical and laboratory methods are so often given in the belief that they are applicable to processes conducted on a large scale, and at high temperatures.

We are told that technical instruction should be kept apart from scientific education, which consists in preparing the student to apply the results of past experience in dealing with entirely new sets of conditions; but it can be shown that there is a whole side of metallurgical teaching which is truly educational, and leads students to acquire the habit of scientific thought as surely as the investigation of any other branch of knowledge.

It is, in fact, hardly possible, in a course of theoretical chemistry, to devote much attention to specific cases of industrial practice in which reactions are incomplete, because they are limited by the presence of bodies that cannot be directly eliminated from the chemical system. Take, for instance, the long series of reactions studied by Plattner, who published the results of his investigations in his celebrated treatise, "Die Metallurgische Röstopprozesse," Freiberg, 1856, whose work I have chosen as a starting-point on account of our presence in South Wales near the great copper smelting district of Swansea. A complex sulphide, of which copper is the main metallic

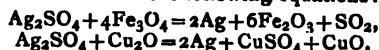
constituent, contains some 50 ounces of silver to the ton. The problem may be supposed for the present to be limited to the extraction of the precious metal from the mass in which it is hidden, and the student deriving his knowledge from an excellent modern chemical treatise would find the case thus stated :—

"Ziervogel's process depends upon the fact that when argentiferous copper pyrites is roasted, the copper and iron sulphides are converted into insoluble oxides, whilst the silver is converted into a soluble sulphate, which is dissolved out by lixiviating the roasted ore with hot water, the silver being readily precipitated from this solution in the metallic state."

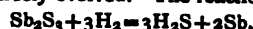
It is certain that if an observant, chemically-trained student visited a silver extraction works, and possessed sufficient analytical skill to enable him to secure evidence as to the changes that occur, he would find a set of facts which his training had not enabled him to predict, and he would establish the existence of a set of reactions to the nature of which his chemical reading had hardly given him a clue. The process to be considered is a simple one, but it is typical, and applies to a large proportion of the 7,000,000 ounces of silver annually obtained in the world from cupriforous compounds. He would be confronted with a ton or more of finely divided material spread in a thin layer over the bed of a reverberatory furnace. Suppose the material is what is known as a complex regulus as imported into Swansea or produced at Freiberg, to which are added rich native sulphides. The mixture then consists of sulphides mainly of iron and copper, with some sulphide of lead, and contains fifty or sixty ounces of silver to the ton, and a few grains of gold. It may also contain small quantities of arsenic and antimony as arsenides, antimonides, and sulpho-salts, usually with copper as a base.

The temperature of the furnace in which the operation is to be performed is gradually raised, the atmosphere being an oxidising one. The first effect of the elevation of the temperature is to distil off sulphur, reducing the sulphides to a lower stage of sulphurisation. This sulphur burns in the furnace atmosphere to sulphurous anhydride (SO_2), and coming in contact with the material undergoing oxidation, is converted into sulphuric anhydride (SO_3). It should be noted that the material of the brickwork does not intervene in the reactions, except by its presence as a hot porous mass, but its influence is, nevertheless, considerable. The roasting of these sulphides presents a good case for the study of chemical equilibrium. As soon as the sulphurous anhydride reaches a certain tension, the oxidation of the sulphide is arrested, even though an excess of oxygen be present, and the oxidation is not resumed until the action of the draught changes the conditions of the atmosphere of the furnace, when the lower sulphides remaining are slowly oxidised, the copper sulphide being converted into copper sulphate mainly by the intervention of the sulphuric anhydride formed as indicated. Probably by far the greater part of the iron sulphide only becomes sulphate for a very brief period, being decomposed into the oxides of iron, mainly ferric oxide, the sulphur passing off. Any silver sulphide that is present would have been converted into metallic silver at the outset, were it not for the simultaneous presence of other sulphides, notably those of copper and of iron, which enables the silver sulphide to become converted into sulphate. The lead sulphide is also converted into sulphate at this low temperature. The heat is now raised still further with a view to split up the sulphate of copper, the decomposition of which leaves oxide of copper. If, as in this case, the bases are weak, the sulphuric anhydride escapes mainly as such; but when the sulphates of stronger bases are decomposed the sulphuric anhydride is to a great extent decomposed into a mixture of sulphurous anhydride and oxygen. The sulphuric anhydride, resulting from the decomposition of this copper sulphate, converts the silver into sulphate,

and maintains it as such, just as, in turn, at a lower temperature, the copper itself had been maintained in the form of sulphate by the sulphuric anhydride eliminated from the iron sulphide. When only a little of the copper sulphate remains undecomposed, the silver sulphate begins to split up, and the furnace charge must therefore be immediately withdrawn, or the whole of the silver sulphate would be converted into metallic silver, partly by the direct action of heat alone, and partly by reactions such as those shown in the following equations :—



If the charge were not withdrawn, the silver would thus be effectually removed from the solvent action of water, and the smelter's efforts would have failed entirely. The charge still contains lead sulphate, which cannot be completely decomposed at any temperature attainable in the roasting furnace, except in the presence of silica, and it is well to leave it where it is if the residue has subsequently to be smelted with a view to the extraction of the gold. The elimination of arsenic and antimony gives rise to problems of much interest, and again confronts the smelter with a case of chemical equilibrium. For the sake of brevity it will be well for the present to limit the consideration to the removal of antimony, which may be supposed to be present as sulphide. Some sulphide of antimony is distilled off, but this is not its only mode of escape. An attempt to remove antimony by rapid oxidation would be attended with the danger of converting it into insoluble antimonates of the metals present in the charge. In the early stages of the roasting it is therefore necessary to employ a very low temperature, and the presence of steam is found to be useful as a source of hydrogen, which removes sulphur as hydrogen sulphide, the gas being freely evolved. The reaction—



between hydrogen and sulphide of antimony is, however, endothermic, and could not, therefore, take place without the aid which is afforded by external heat. The facts appear to be as follows :—sulphide of antimony, when heated, dissociates, and the tension of the sulphur vapour would produce a state of equilibrium if the sulphur thus liberated were not seized by the hydrogen and removed from the system. The equilibrium is thus destroyed and fresh sulphide is dissociated. The general result being that the equilibrium of the system is continually restored and destroyed until the sulphide is decomposed. The antimony combines with oxygen and escapes as volatile oxide, as does also the arsenic, a portion of which is volatilised as sulphide.

The main object of the process which has been considered is the formation of soluble sulphate of silver. If arsenic and antimony have not been eliminated, their presence at the end of the operation would be specially inconvenient, as they give rise to the formation of arseniate and antimoniate of silver, insoluble in water, which may necessitate the treatment of the residues by an entirely different process from that which has hitherto been considered.

It will have been evident that effecting this series of changes demands the exercise of the utmost skill, care, and patience. The operations beginning at a dull red heat, or a temperature of some 500° , are completed at 700° , within a range, that is, of 200° . Judicious stirring has been necessary to prevent the formation of crusts of sulphates, which would impede the reactions, and, as has been shown, an undue elevation of temperature within a very limited range would, at any stage, have been fatal to the success of the operation. It is difficult to appreciate too highly the delicacy of sight and touch which enables an operator to judge by the aid of rough tests, but mainly from the tint of the streak revealed when the mass is rabbled, whether any particular stage has or has not been reached, and it will be obvious that the requisite skill is acquired solely by observation and experiment. The

technical instructor may impart information as to the routine to be followed and the appearances to be observed, but scientific knowledge of a high order can alone enable the operator to contend with the disturbing influences introduced by the presence of unexpected elements or by untoward variations in temperature. In the training of a metallurgist it is impossible to separate education from instruction, and the above description of a very ordinary operation will show the intimate relations between science and practice which are characteristic of metallurgical operations. Practice is dependent on science for its advancement, but scientific workers too often hesitate to attack metallurgical problems, and to devote the resources of modern investigation to their solution, because they are not aware of the great interest of the physical and chemical problems which are connected with many very simple metallurgical processes, especially with those that are conducted at high temperatures.

Proceeding yet one step further, suppose that the copper smelter takes possession of the residual mass, consisting mainly of oxide of copper, he would smelt it with fresh sulphide ores, and obtain, as a slag from the earthy matters of the ores, a ferrous silicate containing some small proportion of copper. The displacement of the copper from this silicate may be effected by fusing it with sulphide of iron, a fusible sulphide of iron and copper being formed which readily separates from the slag. By this reaction some 20,000 tons of copper are added to the world's annual production. Proceeding a step further, suppose the smelter to have reduced his copper to the metallic state. If arsenic had been originally present in the ore, and had not been eliminated entirely in the roasting, extraordinary difficulties will be met with in the later stages of the process, in extracting small quantities of arsenic which resist the smelter's efforts. Copper, moreover, containing arsenic cannot be "overpoled," as the presence of arsenic hinders the reducing action of gases on the copper. The amount of arsenic which the copper smelter has to remove may vary from mere traces up to 1 per cent, and if the copper is destined for the use of the electrical engineer, he will insist on its being as pure as possible, for the presence of a trace of arsenic would materially increase the electrical resistance of the copper, and would be fatal to its use in submarine telegraphy. If, on the other hand, the copper is intended for the maker of locomotive fire-boxes, he will encourage the retention of small quantities of arsenic, as it is found to actually increase the endurance of the copper, and the smelter will in such a case have no inducement to employ the basic furnace lining which Mr. Gilchrist has offered him, nor will he care to use the special methods for the removal of arsenic with which he is familiar. It may all seem simple enough, but the modern process of copper-smelting has been laboriously built up, and has a long and interesting pedigree which may be traced to at least the eighth century, when Geber described the regulus "coarse metal" as being "black mixed with livid," and our familiar "blue metal" as being "of a most clean and pleasant violet colour," and indicated the reasons for the difference.

(To be continued.)

ON NICKEL CARBON OXIDE AND ITS APPLICATION IN ARTS AND MANUFACTURES.

By LUDWIG MOND, F.R.S.

THE existence of a volatile compound of nickel and carbonic oxide was first discovered in my London laboratory in October, 1889, in the course of an investigation on which I was engaged with my assistants, Dr. Carl Langer

and Dr. Friedrich Quincke, into the remarkable property of metallic nickel to induce, at the comparatively low temperature of 350° C., the complete dissociation of carbonic oxide into carbon and carbonic acid, which, according to Victor Meyer and Carl Langer, by the application of heat alone remains incomplete at a temperature of 1690° C.

A very small quantity of nickel can effect the dissociation of a large quantity of carbonic oxide, and becomes converted into a very voluminous black mass containing varying quantities of carbon up to 85 per cent. This mass takes fire on exposure to air, so that we had to cool it under exclusion of air for the purpose of analysis, which was done in a slow current of carbonic oxide gas. This gas was subsequently led into a Bunsen burner, so as to keep it out of the atmosphere of the room. In this way we observed that when the cooling had proceeded to a certain point (about 150° C.), the Bunsen flame became luminous and remained so, and even became intense, down to ordinary atmospheric temperature. When the gas before entering the burner was heated in a glass tube a metallic mirror was obtained, while the luminosity of the flame disappeared.

We were at first inclined to refer this phenomenon to the presence in the nickel of an unknown element, perhaps to Krüss and Schmidt's Gnomium, which at this time still haunted chemical literature. The metal of the mirror, however, gave all and every one of the reactions of nickel with remarkable brilliancy, and an approximate determination of the atomic weight came out so nearly to the very carefully-determined figure of Russel for nickel (58.58 as compared with 58.74), that there could be no doubt about its identity with our well-known old friend, whose character as a simple body, called in question by Krüss and Schmidt, was thus rehabilitated.

In repeating the experiment with carbonic oxide, quite free from hydrogen and moisture, and only contaminated with nitrogen, the same result was obtained. After removing the carbonic oxide by cuprous chloride, and heating the residual gas to 180° in aniline vapour, at which temperature nickel, quite free from carbon, is separated, we found the volume of the gas to expand considerably, and the gas to contain only nitrogen and carbonic oxide. It was thus evident that we had obtained a volatile compound of nickel and carbonic oxide, which, on heating, dissociated into its constituents. The increase of volume proved that one volume of gas yielded four volumes of carbonic oxide, and the determination of the amount of nickel deposited and the carbonic oxide formed led to a proportion of four equivalents of carbonic oxide to one of nickel. To further study the properties of this compound it was necessary to produce larger quantities, which took us a long time to accomplish. By preparing the nickel in a very fine state of division, at the lowest possible temperature, by reducing the oxide, or, better still, the oxalate, in a current of hydrogen at about 400° C., and by carefully purifying and regulating the current of carbonic oxide, we succeeded at last in forming the compound quite readily, and in obtaining a gas sufficiently rich that on passing it through a refrigerator, cooled by ice and salt, we condensed the compound to a liquid.

This liquid is colourless, mobile, highly refracting, possesses a characteristic odour, and is very volatile. It is soluble in a large number of organic liquids, such as alcohol, ether, chloroform, benzole, petroleum, tar oils, &c. It boils at 43° C. at 751 m.m. pressure without decomposition, and evaporates rapidly at ordinary temperature in a current of other gases. The specific gravity is 1.3185 at 17° C.; at -25° it solidifies, forming needle-shaped crystals; the pure vapour explodes when suddenly heated to above 60°, and even when the tube containing it is scratched roughly with a file. A mixture of the vapour with air explodes violently on the application of a flame. Both the liquid and the vapour are poisonous, the latter approximating carbonic oxide in this respect. According to an investigation kindly undertaken by Prof.

* Read before the British Association for the Advancement of Science, Cardiff Meeting, 1891, Section B.

McKendrick, the liquid dissolved in chloroform produced, when injected subcutaneously in extremely small doses in rabbits, an extraordinary reduction of temperature, amounting in some cases to 12° C.

Careful determinations of the quantity of nickel contained in the liquid, made by introducing a weighed quantity into chlorine water and precipitation of the nickel from the resulting solution, led to figures agreeing very closely with the formula $\text{Ni}(\text{CO})_4$, viz., 34.33 and 34.26 per cent of nickel, the formula requiring 34.28. The vapour density determined by Victor Meyer's method at 50° was found equal to 6.01; the formula $\text{Ni}(\text{CO})_4$ requires 5.89.

The compound is chemically very inactive; generally speaking, it only reacts with substances having a considerable affinity for nickel, such as the halogens, sulphur, oxygen, and oxidising substances, which combine with the nickel and liberate carbonic oxide. Chlorine and bromine when used in excess also enter into combination with the carbonic oxide. Sulphur in the dry state forms a sulphide of nickel corresponding to the formula Ni_2S_3 , and dissolved in bisulphide of carbon it forms a sulphide containing more sulphur, but of varying composition. Selenium acts similarly but very slowly. Tellurium shows hardly any action. Metals (even potassium) are not acted upon.

Alkalies and acids (even strong hydrochloric acid) produce no change except they are oxidising agents, such as nitric acid and aqua regia. With metallic salts no reaction is obtained unless they have oxidising properties as hypochlorites, which form a higher oxide of nickel, or they are capable of giving off sulphur, such as hypsulphites and bisulphites.

We have tried in vain to substitute the carbonic oxide in this compound by other bivalent groups, or to introduce the carbonic oxide by means of this compound into organic substances. Our experiments in this direction have covered a very wide range and have included, amongst others, the following:—hydroxylamine hydrochloride, phenylhydrazine hydrochloride, hydroxylamine, dichloroacetic acid, tetrabromophenolbromide, ethylchloride, and aceto-acetic-ether, but in no single instance have we succeeded in obtaining the desired result.

On exposure to moist or dry air a flocculent substance, which varies in colour from a light green to a dark brown, is very slowly formed. This substance dissolves completely in dilute acids with evolution of carbonic acid; numerous analyses have not led to a definite proportion between Ni and CO_2 in this compound. On heating it to dull red heat it turns black. Prof. Berthelot, in a paper recently communicated to the French Academy of Sciences, assumes that this black colour is produced by the separation of carbon, and bases upon this an argument that the compound is of a complex composition, and that the nickel carbon oxide, on exposure to air, behaves like a real compound radical analogous to organo-metallic radicals. As, however, the black substance so obtained dissolves in dilute acids without leaving any residue, and as an exactly similar black substance is obtained by heating precipitated nickel carbonate, this argument does not seem to be conclusive, and I must regret that Professor Berthelot has not substantiated so important a conclusion by a complete analysis of the black substance.

Prof. Berthelot describes in the same paper a very beautiful blue compound obtained by treating nickel carbon oxide with nitric oxide. Unfortunately he does not publish an analysis of this beautiful substance either, so that until he has done so we are unable to judge of its bearing on the constitution of nickel carbon oxide.

With a view to elucidate this constitution I have, in conjunction with Prof. R. Nasini, of Rome, studied the physical properties of the liquid, more especially its refraction and dispersion. The details of this investigation have been communicated to the Accademia dei Lincei at Rome, and have also been published in the *Journal für Physikalische Chemie*.

We have determined the freezing-point of a dilute solution in benzol containing 4.8991 per cent, and have found the coefficient of diminution 0.2776, corresponding to a molecular weight of 176.5; while nickel carbon oxide requires 170.6. The mean cubical coefficient of expansion between 0° and 36° C. we found equal to 0.001853, which is one of the highest coefficients of expansion yet found for any liquid, and is only slightly exceeded by ethylic ether, ethyl chloride, and silicium tetrachloride. We have determined the refraction, and the dispersion for the lines α , β , and γ of hydrogen, and for the lines of lithium, sodium, and thallium, at three different temperatures, and have found both to be very high. The dispersion is about the same as carbon disulphide. The refraction varies very much with the temperature, the amount of variation being very nearly equal to that of carbon disulphide. The refraction for the D line at 10° C. is 1.45843.

According to Gladstone's formula this leads to the specific refraction of 0.3437, and the molecular refraction of 58.63. Under the supposition that the group CO had the same value in our compound which results from the sum of the atomic refraction of carbon and that of the bivalent oxygen molecule in organic compounds, which is the more probable, as the group CO shows very nearly the same molecular refraction in compounds of the most different constitution, such as oxalic acid, ketones, and carbonyldichloride, the atomic refraction of nickel would come out equal to 25.02. This figure is very much higher, nearly two and a half times as high as it is in nickel salts, in which it has been found by Gladstone to be about 10; and about four times as high as the atomic refraction of metallic nickel as determined by Kundt and Dubois and Rubens, viz. about 6.

This difference of the atomic refraction of nickel in our compound and in its ordinary combinations is by far greater than that found in any other element. According to the generally accepted view, such differences are due to the element exercising a larger number of valencies, and are proportional to the number of valencies thus exercised. Nickel is generally bivalent. Its very high atomic refraction in nickel carbon oxide would thus lead to the conclusion that in this compound the nickel exercises a considerably higher valency than two, and that it has probably reached its maximum of saturation foreseen by Mendeléeff, who placed this metal in the eighth group of his Periodic System, to be equal to eight; so that the constitution of our compound would be a simple combination of one octovalent equivalent of nickel with four bivalent equivalents of carbonic oxide, or that of nickel tetracarbonyl.

All that we definitely know of the chemical properties of the compound is in accord with this view of its constitution.

A determination of the magnetic rotary power of the compound kindly made by Dr. W. H. Perkin has shown this to be quite as exceptional as its refraction, and, with the exception of phosphorus, greater than any substance he has yet examined.

Professor Quincke, of Heidelberg, has had the kindness to investigate the magnetic properties of the liquid. He found the constant of diamagnetism at—

$$16^\circ \text{C. } k = -3.131 \times 10^{-10}$$

for magnetic fields of 6000 to 14,000 C.G.S. units. This is nearly the same as the constant for ethylic ether $= -3.218 \times 10^{-10}$.

The liquid is an exceptionally bad conductor of electricity. Up to 40 volts no current was observed to pass, the electrodes of 1 sq. c.m. area being 1 c.m. apart.

The highly interesting properties of nickel carbon oxide naturally led us to try whether we could not obtain similar compounds of other metals. It seemed a foregone conclusion that cobalt, in every respect so much like nickel, must give an analogous compound. It seemed probable that other metals of the eighth group, and those standing near to nickel in other groups, would also com-

bine with carbonic oxide. We tried a large number of elements, including osmium, palladium, ruthenium, rhodium, iridium, and manganese, by acting upon them in the finely divided state with carbonic oxide gas over a wide range of temperature. We tried it by double decomposition with numerous compounds, including zinc ethyl and mercury methyl; but, with one sole and single exception, without success.

This sole exception is iron. This metal, too, had for a long time given us negative results; but by preparing it at the lowest possible temperature by reduction of the oxalate in a current of hydrogen, and by acting upon this at about 80° C. with a very slow current of very pure carbonic oxide, I succeeded at last, in conjunction with Dr. F. Quincke, in obtaining evidence that a volatile compound of this element with carbonic oxide exists. The gas obtained imparted a yellow tinge to a Bunsen flame, and yielded slight metallic mirrors composed of pure iron. The quantity of the iron compound in the gas was, however, extremely small. By passing the gas through heavy tar oils, in which the compound is soluble, but from which it cannot be separated by fractionation, as it decomposes on heating the solution into iron and carbonic oxide before it volatilises, and by determining the iron and carbonic oxide so obtained, we ascertained, as far as the very small quantities of the substance at our disposal would allow, that it contained iron and carbonic oxide in the proportion of 1 equivalent of iron to 4.126 of carbonic oxide, or very nearly 1 to 4.

Since these results were communicated to the Chemical Society (18th June, 1891) I have continued the study of this body, in collaboration with Dr. Carl Langer, and we have arrived at obtaining it as an amber-coloured liquid, which, on standing, deposits tabular crystals of a darker colour, and solidifies entirely below -21° C. to a mass of needle-shaped crystals. It boils at 102° C., but leaves a small quantity of green-coloured oil behind.

We have made several analyses and vapour density determinations, but are not yet certain whether we have a pure substance in hand or a mixture of several iron carbonyls. We hope to be able very shortly to publish a full account of this interesting substance, which differs considerably in its chemical behaviour from nickel carbon oxide.

The fact that under ordinary circumstances nickel alone is acted on when a mixture of this metal with any other metallic or mineral substances is treated by carbonic oxide gas, led me to institute experiments to ascertain whether it would not be possible by means of carbon oxide to extract nickel direct from its ores, and such metallurgical products as nickel speiss and nickel matte. As the nickel is volatilised at the ordinary temperature in the form of a vapour disseminated through other gases from which it can be deposited without first condensing the nickel compound by simply heating these gases to the moderate temperature of 200° C., as it is thus obtained in the form of bright coherent masses of great purity, as the carbonic oxide used is completely liberated and can be employed over and over again, and as small quantities of the poisonous nickel compound which may escape decomposition would thus never leave the closed apparatus in which the process would be carried out, it seemed probable that such a process might be capable of industrial application, and might prove more economical than the very complicated operations metallurgists have now to resort to to produce tolerably pure nickel.

Experiments carried out under my instructions by Dr. Langer with a great variety of nickel ores from all parts of the world, containing from 4 to 40 per cent of nickel, as well as a number of samples of nickel speiss and nickel matte, have proved that as long as the nickel is combined with arsenic or sulphur the process is entirely successful on a laboratory scale. In the majority of cases I have been able to extract the nickel almost completely in three to four days.

Such ores or matte or speiss have in the first instance

to be calcined, so as to convert the nickel completely into oxide. The mass is then reduced in a current of hydrogenous gases, in practice water-gas, at a temperature of 450° C. It is cooled down to ordinary temperature, and treated with carbonic oxide in a suitable apparatus. For this purpose any good apparatus for treating solids by gases, of which a great number are in common use, will answer. Methodical apparatus moving the reduced ore in opposite direction to the current of carbonic oxide, at the same time exposing fresh surfaces, facilitate the operation. After a certain time the action of the carbonic oxide upon the nickel becomes sluggish. The mass is then heated to about 350° C. in a current of carbonic oxide, which regenerates the activity of the nickel. This may be done in the same apparatus, but it is preferable to use a separate apparatus connected with the first, and from which it is returned to the first by mechanical means, so that each apparatus can be kept at the same temperature. The carbonic oxide gas can be employed dilute, as it is obtained from gas-producers; but, since it is continuously recovered, a purer gas—such as can be cheaply prepared by passing carbonic acid through incandescent coke—is more advantageous, as it extracts the nickel more quickly and requires smaller apparatus. The gas charged with the nickel compound leaving the apparatus is passed through tubes or chambers heated to about 200° C., in which the nickel is deposited. The gas leaving these tubes is returned to the first apparatus and circulates continuously. From time to time the nickel is removed from the tubes in which it has been deposited. To facilitate this operation thin nickel sheets, bent to fit the tubes, are inserted, on which the nickel deposits, and which are easily taken out. The metal so obtained is almost chemically pure; only very rarely, in the case of certain ores, it is slightly contaminated with iron. Its density is equal to that of ordinary sheet nickel. Its mechanical properties still await investigation.

As the nickel is deposited in perfectly coherent films upon heated surfaces exposed to the gas containing the nickel carbon oxide, I have found it possible to produce direct from such gas articles of solid nickel or goods plated with nickel resembling in every way those obtained by galvanic deposition of metals, and reproducing with the same exactitude and fineness any design upon such articles.

This result can also be obtained by immersing heated articles in a solution of nickel carbon oxide in such solvents as benzol, petroleum, tar oils, &c., or by applying such solution to the heated articles with a brush or otherwise.

These processes open up a wide perspective of useful application, considering the many valuable properties of nickel, especially its power of resisting atmospheric and other chemical influences.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 76).

XIX.—Calcium.

1. PRECIPITATION as sulphate occurs most frequently. It separates as $\text{CaSO}_4 + 2\text{H}_2\text{O}$ in prismatic crystals of the monoclinic system, which, in strongly acid liquids, fall down in thin, acicular crystals, entangled together in bushes and stars; in neutral solutions, or in the presence of acetic acid, they take the appearance of natural crystals of selenite, of the form of parallelograms, with an acute angle of 65° 36', and as swallow-tailed twin crystals, which in very dilute solutions, when concentrated by

* Zeit. Anal. Chemie.

evaporation, accumulate along the margin. The limit of the reaction is about 0.00004 m.grm. Ca.

Hydrochloric and sulphuric acids diminish the sensitiveness, and in very dilute calcium solutions large quantities of alkaline salts must be avoided. Aluminium, chromium, and iron chlorides delay the reaction, and cause the production of small squares and granules of 10 micro. This may be remedied by boiling up with sodium or ammonium acetate. Boric acid interferes in a similar manner.

2. With potassium and sodium double tartrate and a little acetic acid, we obtain crystals of the form of strontium tartrate which often reach 80 micro. in length and 60 micro. in thickness. Limit of the reaction at 0.00003 m.grm. Ca.

Barium and strontium must be removed by means of sulphuric acid. Barium would disturb the formation of crystals, and strontium would yield mixed crystals with calcium. A separation of crystals of gypsum does not interfere. They re-dissolve, and in their place there appear large crystals of tartrate. In this form the reaction can be used as a check upon No. 1. Boric acid prevents the formation of crystals and occasions a finely granular turbidity. The action of aluminium, chromium, and iron chlorides is similar.

3. No precipitate is obtained in solutions of calcium salts. An excess throws down quadratic tables of a sparingly soluble double salt (20–25 micro.). A simultaneous addition of ammonium chloride causes the precipitate to appear in very dilute solutions. The limit of the reaction is at 0.000015 m.grm. Ca. Salts of strontium are not precipitated, barium falls only from very concentrated solutions in pale yellow rhombohedra (soluble in 38 parts of water).

4. With oxalic acid we obtain a very finely crystalline precipitate. In order to obtain at common temperatures crystals which are distinctly visible, the sample must be made moderately acid, preferably with nitric acid. The retarding action of the acid is less decisive with calcium than with strontium. The crystals of calcium oxalate are sharply-formed tetragonal pyramids of 12–25 micro. Limit of the reaction at 0.00006 m.grm. Ca. Boric acid and aluminium, chromium, and iron chlorides have little influence upon the precipitation. The influence of stannic chloride is much less manifest than with the barium and strontium oxalates.

5. Sodium bicarbonate occasions in solutions of calcium salts the formation of colourless rhombohedra of calcium carbonate, which polarise strongly. They increase rather sluggishly up to 25 micro. Ammonium carbonate produces a pulverulent precipitate which is gradually transformed into rhombohedra. The reaction is very sensitive, and it is not interfered with by aluminium, chromium, and iron. It is rather tedious, and it is useless in presence of magnesium, strontium, and barium.

XX.—Lead.

1. With hydrochloric acid. In the course of analytical operations lead is often unintentionally separated out as lead chloride, and it is then not always easy to recognise. From neutral solutions it is deposited in large rods or flat ridges, which often adhere together in the shape of an X and display ramifications. Lead chloride is soluble in 135 parts of water, its solubility being increased by nitric acid. Limit of the reaction at 0.0003 m.grm. Pb.

Potassium chloride causes a formation of thread-shaped rudimentary crystals. Ammonium chloride may entirely prevent the formation of crystals. If tin, bismuth, and antimony chlorides are present, water and hydrochloric acid dissolve only a part of the lead.

2. Potassium iodide can be used with advantage as a check upon the precipitation of lead chloride. Lead iodide generally falls down as a yellow crystalline powder. From its solution in hot water it crystallises in lemon-yellow six-sided tablets of 20 micro. Limit of the reaction 0.0002 m.grm. Pb.

In acid solutions of lead, antimony, and bismuth, potassium iodide determines not a yellow but an orange, or even a scarlet precipitate. Heating with dilute hydrochloric acid decomposes it and causes lead oxide to crystallise.

3. Lead sulphate can be caused to crystallise by slow evaporation with nitric acid. It forms acute rhombs of 10 micro., the edges of which are often indented, and six-sided tablets. Limit of the reaction at 0.00004 m.grm. Pb.

4. Sodium bicarbonate precipitates immediately, and ammonium carbonate in two minutes, ramified rods of 12–20 micro., the form of which is very striking and characteristic. Limit of the reaction at 0.00006 m.grm. Pb.

Oxalic acid throws down grains and crosses of 20–30 micro. (in presence of stannous chloride rosettes of 100 micro.)—but from hot solutions rectangular rods of 40–60 micro. The reaction has little value. Its limit is at 0.0002 m.grm. Pb.

Potassium bichromate throws down from solutions of lead a yellow powder of $PbCrO_4$. Its finely granular texture and opacity render this precipitate unfit for microscopic observation.

XXI.—Copper.

1. With potassium nitrite and lead acetate. Black cubes with sharp edges of 10–25 micro., which, by re-crystallisation, can be brought to 70 micro. In thin plates translucent, orange, or brown. Limit of reaction 0.00003 m.grm. Cu.

The sample to be tested for copper is placed in a drop of a concentrated solution of potassium nitrite, supersaturated with acetic acid, and a minute granule of lead acetate is added. A turbidity ensues, and in one to two minutes cubes of 10–25 micro. are formed. The new copper compound—the composition of which probably corresponds to that of potassium-nickel-lead nitrite—is decomposed by hot water. It is partially soluble in an acidified solution of potassium nitrite; another portion is decomposed, and is re-formed on cooling. Barium and strontium give analogous compounds which do not crystallise so well.

2. With potassium ferrocyanide there are obtained from ammoniacal solutions of copper during the evaporation of the ammonia, yellow crystalline structures generally feathery and dendritic. They gradually become red on exposure to the air, or immediately on the addition of acetic acid. Limit of reaction 0.0001 m.grm. Cu.

3. Ammonium mercuri-sulphocyanide precipitates from slightly acid solutions of copper brownish green crystals, which in form resemble those of cobalt-mercuric sulphocyanide. If the solution contains both metals, cobalt is separated first and then copper. No mixed crystals are formed. The limit of this characteristic but rather tedious reaction is 0.0001 m.grm. Cu.

4. Potassium iodide precipitates from concentrated solutions of cupric salts white pulverulent cuprous iodide, with a simultaneous separation of iodine. To dilute solutions there must be added at the same time a reducing agent (sodium sulphite and sulphuric acid). The finely granular texture of this precipitate makes the reaction inconvenient. Limit at 0.00005 m.grm. Cu.

XXII.—Mercury.

a. *Mercurous Salts.*—1. Hydrochloric acid throws down fine needles which quickly break up to minute granules of a square section. Mercurous chloride is blackened by ammonia. For its examination the precipitate should be illuminated from below. Limit 0.00025 m.grm. Hg.

2. Potassium bichromate produces in mercurous solutions containing a considerable quantity of free nitric acid a fine red pulverulent precipitate, which in the acid liquid is transformed (not invariably) into cruciform red crystals of 10–15 micro. Limit 0.0005 m.grm. Hg.

b. *Mercuric Salts.*—1. Potassium iodide precipitates

from mercuric solutions a scarlet deposit consisting of quadratic tablets and pyramids of a square section. In an excess of the reagent it dissolves to a colourless liquid. An addition of copper sulphate reproduces it more beautifully than before, unless a large excess of potassium iodide is present. Limit of reaction 0.000075 m.grm. Hg.

2. Stannous chloride reacts upon mercuric chloride very sensitively, but for microscopic use it is less to be recommended than potassium iodide, as the precipitate of mercurous chloride is very finely granular. Limit of the reaction 0.00005 m.grm. Hg.

3. Ammonium sulphocyanide throws down from concentrated solutions of mercuric salts a crystalline colourless precipitate soluble in excess. If cobalt nitrate is added there appear the dark blue crystals of cobalt-mercuric sulphocyanide, described under Cobalt 2. In very dilute solutions they appear at the margin of the drop during evaporation. Limit at 0.00004 m.grm. Hg. Lead and bismuth must not be present.

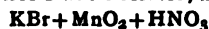
(To be continued).

CORRESPONDENCE.

SEPARATION OF THE HALOGENS.

To the Editor of the Chemical News.

SIR,—In studying the halogens some time ago I found that by putting $KI + MnO_2 + C_2H_4O_2$ into a test-tube and slightly heating, free I was liberated, and that—



slightly heated yielded free Br. I then put together a crystal of KI, KBr, and $NaCl + MnO_2 + C_2H_4O_2$, and slightly heated, and obtained free I. After driving it all off I added a little HNO_3 , and upon heating obtained free Br, which was driven off also, then cooled the tube, and cautiously added H_2SO_4 , and heated, when free Cl came away, known by smell, colour, and bleaching of moist litmus. The experiment is interesting from the fact that it is held that these three elements cannot be recognised in the presence of one another.—I am, &c.,

MATTHEW FORBES.

12, Bell Street, Dundee.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 5, August 3, 1891.

Combustion and Formation-Heats of the Nitrobenzenes.—MM. Berthelot and Matignon.—Thermochemical determinations.

Improvements introduced in the Manufacture of Soda-Water. Arrangement of the Syphon.—M. de Pietra-Santa.—The water used is taken from the springs of the Dhuis and the Vanne, and is submitted to repeated filtration. The gasification is effected by means of liquid carbonic acid. The fittings of the syphon are formed of pure tin to the total exclusion of lead.

The Expansion of Phosphorus and its Change of Volume at the Melting-Point.—A. Leduc.—According to the author, phosphorus expands almost regularly up to the point of fusion, which is at 44.2° of the mercurial thermometer, and consequently at 44.1° of the normal thermometer. He has followed the expansion of the liquid phosphorus up to 50° , and then down to 26° , at which it solidified.

Study on the Chemical Neutralisation of Acids and Bases by Means of their Electric Conductivities.—Daniel Berthelot.—Potassa, a powerful base, yields with hydrochloric acid, acetic acid and phenol, compounds having conductivities near to each other, behaving like true salts, being stable in solution, and not decomposed by water. Ammonia forms with hydrochloric and acetic acid stable compounds, but with phenol it forms an instable compound less conductive than the neutral salts, and in great part dissociated by water. Aniline yields with hydrochloric acid a stable compound, which is a good conductor; with acetic acid an instable compound, moderately conductive; with phenol it forms merely a non-conductive mixture without a trace of combination.

Action of Phenylhydrazine upon the Phenols.—Alphonse Seyewetz.—A fairly great number of phenols react with phenylhydrazine. Among them the diatomic phenols seem to form such compounds most readily. Many analogous compounds of aniline and phenylhydrazine (aniline phenates) are known, but they do not correspond exactly with those furnished by phenylhydrazine. Several phenols combine very readily with aniline, but not with phenylhydrazine. Certain phenylhydrazine phenates are very easily formed, whilst the corresponding aniline phenates are often formed with great difficulty.

Action of Poisons upon the Germination of the Seeds of the Plants by which they are Produced.—Ch. Cornevin.—When a phanerogamous plant elaborates a poison by any part other than its seeds, if such poison is brought in contact for a sufficient time with the seeds, it sometimes hinders germination, e.g., nicotine, and sometimes favours it as in the case of opium. Soil saturated with such substances, is either, according to the species, unfit for the development of the vegetable germ, or promotes it like a suitable manure.

Zeitschrift für Analytische Chemie.
Vol. xxix., Part 6.

Recognition of a Fraudulent Addition of "Ruben-kraut" in Rhenish Obst-Kraut.—(See page 74).

A Cheap Ebullioscope.—Benevolo (*Weinlaube*).—This instrument cannot be intelligibly described without the accompanying cut.

Detection of Sugar or Treacle in Roasted Coffee.—A. Stutzer and O. Reitmayr (*Zeit. Angew. Chemie*).—Already inserted.

The Sophistications of Safron.—G. Kuntze and A. Hilger (*Archiv für Hygiene*).—Pure saffron should not contain more than 8 per cent of ash. Its ash yields 13.53 per cent of phosphoric acid, whilst safflower (*Carthamus tinctorius*) contains only about 2 per cent, and the flowers of *Calendula* 0.37 per cent.

Chemical Examination of Pepper.—H. Weigmann (*Repert. Anal. Chemie*).—This author is criticised as having in his researches omitted certain known and important precautions.

Detection and Estimation of Starch in Liquids containing Dextrine.—G. Burkard (*Chemiker Zeitung*).—Already inserted.

Detection of Magenta in Extracts of Dye-Woods.—F. Fairley.—From the *Jour. Soc. Chem. Ind.*

Determination of Phenols in Carbolic Soap.—A. H. Allen.—From the *Analyst*.

The Presence of Alcohol in Commercial Ethyl-Ether.—Th. Poleck and K. Thümmel (*Archiv. de Pharm.*).—Already inserted.

Determination of Paraffin, Ceresine, and Mineral Oils in Fats and Waxes.—F. M. Horn (*Zeit. Angew. Chemie*).—Already inserted.

Determination of Resin Oils in Mineral Lubricants.—L. Storch (*Chemiker Zeitung*).—Already inserted.

Detection of Cotton-Oil in Lard.—A. Bujard and J. Waldbauer (*Zeit. Angew. Chemie*).—Already inserted.

Rape Oil.—Reimer and Will (*Deutsch. Chem. Gesell.*).—Already inserted.

Recognition of Sesame Oils.—W. Bishop.—From the *Journal de Pharm. et de Chimie*.

Determination of Castor Oil in Oily Mixtures.—J. Braun (*Rundschau*).—The author submits a weighed sample to dry distillation in a tared distilling flask capable of holding 100 to 200 c.c. The heat is rapidly raised to 265°. After heating for 15–30 minutes, the mass suddenly swells up, when the flame is removed; the contents of the flask are allowed to cool from 50 to 60°, and then washed successively with 5 per cent ammonia, water, alcohol, and ether, shaking up the mass well. The weight of the residue if multiplied by 1.63 gives the weight of the castor oil.

Examination of Commercial Cocaine.

Determination of Colchicine in Colchicum Seeds.—Kremel (*Pharm. Post and Chemiker Zeitung*).—For these two papers we must refer to the original.

Distinction between Common Turpentine and Larch Turpentine.—E. Hirschsohn (*Pharm. Zeit. für Russland*).—If a few drops of common turpentine in a test-tube are covered with 5 parts ammonia of specific gravity 0.96, the turpentine forms a milky emulsion and soon gelatinises. Larch, otherwise known as Venice turpentine, remains apparently unaffected, but if constantly stirred up it becomes a solid, colourless mass.

Determination of the Value of Strychnos Seeds and Preparations of Strychnine.—H. Beckurtz (*Archiv. der Pharm.*).—The author recommends the method of Dietrich given in this journal, vol. xxix., p. 231.

Valuation of Pomegranate Root Bark.—E. Aweng (*Pharm. Zeitung*).—For this paper the reader is referred to the original.

Recognition and Determination of Reducing Substances, Carbohydrates, and Sugars on Animal Liquids.—A compilation from a number of sources not admitting of abstraction.

Absorption Spectrum of Methæmoglobine and Sulphmethæmoglobine.—T. Araki (*Zeit. Physiol. Chemie*).—Of the four absorption bands ascribed to methæmoglobine, Araki considers only band I. in the red as characteristic. Bands II. and III. lying between D and E in the green are ascribed to an admixture of oxyhæmoglobine, and can be converted by cautious reduction (preferably by putrefaction in a sealed tube) into the broad absorption band of reduced hæmoglobine. In this case the solution shows the spectrum of hæmoglobine, which, on shaking with air, passes into oxyhæmoglobine. A solution of blood turned green by the introduction of hydrogen sulphide shows absorption beginning near C, and extending almost to D, interrupted by a lighter zone in the middle. Between D and E the solution, if oxygen can enter, shows the absorption bands of oxyhæmoglobine.

The Atomic Weight of Tellurium.—B. Brauner.—From the *Journal of the Chemical Society*.

The Atomic Weight of Zirconium.—G. H. Bailey.—From the *CHEMICAL NEWS*.

The Atomic Weight of Iridium.—A. Joly.—From the *Comptes Rendus*.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) of the Cardiff Meeting of the British Association:—

President—Professor W. Chandler Roberts-Austen, C.B., F.R.S., F.C.S.

Vice-Presidents—Sir F. A. Abel, C.B., D.C.L., D.Sc., F.R.S.; W. Crookes, F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; Professor G. D. Liveing, M.A., F.R.S.; Professor H. M'Leod, F.R.S., F.C.S.; Professor R. Meldola, F.R.S.; Ludwig Mond, F.R.S., F.C.S.; Professor C. M. Thompson, M.A., D.Sc.

Secretaries—C. H. Bothamley, F.C.S., F.I.C.; H. Forster Morley, M.A., D.Sc., F.C.S. (*Recorder*); Dr. W. W. J. Nicol, M.A., F.R.S.E.; G. S. Turpin, M.A., D.Sc.

Committee—A. H. Allen; R. W. Atkinson; J. Brown; Professor W. R. Dunstan; A. E. Fletcher; G. Gladstone; A. Vernon Harcourt, F.R.S.; H. Heywood, J.P.; H. C. Jenkins; Dr. H. R. Mill; D. H. Nagel, M.A.; Dr. S. Rideal; Professor H. Lloyd Snape; T. Turner.

The Papers brought before the Section were as follows:—

President's Address.

Report of the Committee on International Standards for the Analysis of Iron and Steel.

Report of the Action of Light upon Dyed Colours.

Report on the Influence of the Silent Discharge of Electricity on Oxygen and other Gases.

Report on the Bibliography of Solution.

Report on the Nature of Solution.

Report on the Bibliography of Spectroscopy.

Report of the Committee on the Formation of Haloid Salts.

Prof. Vivian B. Lewes.—The Spontaneous Ignition of Coal.

Ludwig Mond, F.R.S.—Nickel Carbon Oxide and its Application in Arts and Manufactures.

W. Crookes, F.R.S.—Electrical Evaporation of Metals and Alloys.

T. Turner.—The Cause of the Imperfection of the Surface of Rolled Copper Alloys.

Prof. Roberts-Austen, F.R.S.—Certain Pyrometric Measurements, and Methods of Recording them.

A. P. Laurie.—On the Existence of a Compound in Alloys of Gold and Tin.

A. Vernon Harcourt, F.R.S., and F. W. Humphery.—The Relation between the Composition of a Double Salt and the Composition and Temperature of the Liquid in which it is Formed.

Dr. J. H. Gladstone, F.R.S., and W. Hibbert.—Some Experiments on the Molecular Refraction of Dissolved Electrolytes.

Prof. H. M'Leod, F.R.S.—The Action of Heat on Alkaline Hypochlorites.

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THE CHEMICAL NEWS.

VOL. LXIV., No. 1658.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

By Professor W. C. ROBERTS-AUSTEN, C.B., F.R.S.,
President of the Section.

CARDIFF, 1891.

(Concluded from p. 108.)

(3). THE foregoing instances have been given to indicate the general nature of metallurgical chemistry. It will be well now to show how the great advances in metallurgical practice have been made in the past, with a view to ascertain what principles should guide us in the future.

It is a grave mistake to suppose that in industry, any more than in art, national advance takes place always under the guidance of a master possessed of some new gift of invention; yet we have been reminded that we are apt to be reverent to these alone, as if the nation had been unprogressive, and suddenly awakened by the genius of one man. The way for any great technical advance is prepared by the patient acquisition of facts by investigators of pure science. Whether the investigators are few or many, and consequently whether progress is slow or rapid, will depend in no small measure on the spirit of the nation as a whole. A genius whose practical order of mind enables him to make some great invention suddenly arises, apparently by chance, but his coming will, in most cases, be found to have "followed hard upon" the discovery by some scientific worker of an important fact, or even the accurate determination of a set of physical constants. No elaborate monograph need have reached the practical man—a newspaper paragraph, or a lecture at a Mechanics' Institute may have been sufficient to give him the necessary impulse; but the possessors of minds which are essentially practical often forget how valuable to them have been the fragments of knowledge they have so insensibly acquired that they are almost unconscious of having received any external aid.

The investigating and the industrial faculty are sometimes, though rarely, united in one individual. Rapid advance is often made by those who are untrammelled by a burden of precedent, but it should be remembered that though the few successes, which have been attained in the course of ignorant practice, may come into prominence, none of the countless failures are seen.

I would briefly direct attention to certain processes which have been adopted since the year 1849, when Dr. Percy presided over this Section at Birmingham, a great metallurgical centre. In that year the President of the Association made a reference to metallurgy, a very brief one, for Dr. Robinson only said "the manufacture of iron has been augmented six-fold by the use of the puddling-furnace and the hot-blast, both gifts of theory"; and so, it may be added, are most of the important processes which have since been devised. Take the greatest metallurgical advance of all, the Bessemer process, which has probably done more than any other to promote the material advance of all countries. It was first communicated to the world at the Cheltenham Meeting of the British Association, 1856. Its nature is well known, and I need only say that it depends on the fact that when air is blown through a bath of impure molten iron, sufficient heat is evolved by the rapid combustion of silicon, manganese, and carbon to maintain the bath fluid after these elements have been eliminated, there being no external source of heat, as there is in the puddling furnace or the refinery hearth. We have recently been told that

at an early and perilous stage of the Bessemer process confidence in the experiments was restored by the observation that the temperature of the "blown" metal contained in a crucible was higher than that of the furnace in which it was placed. The historian of the future will not fail to record that the way for the Bessemer process had been prepared by the theoretical work of Andrews, 1848, and of Favre and Silbermann, 1852, whose work on the calorific power of various elements showed that silicon and phosphorus might be utilised as fuel, because great heat is engendered by their combustion.

The basic process for removing phosphorus, a process of great national importance, the development of which we owe to Thomas and Gilchrist, is entirely the outcome of purely theoretical teaching, in connection with which the names of Gruner and Percy deserve special mention. In the other great group of processes for the production of steel, those in which Siemens's regenerative furnace is employed, we have the direct influence of a highly-trained theorist, who concluded his address as President of this Association in 1882 by reminding us that "in the great workshop of nature there is no line of demarcation to be drawn between the most exalted speculation and commonplace practice." The recent introduction of the method of heating by radiation is, of course, the result of purely theoretical considerations.

The progress in the methods of extracting the precious metals has been very great, both on the chemical and engineering sides, but it is curious that in the metallurgy of gold and silver, many ancient processes survive which were arrived at empirically—a noteworthy exception being presented by the chlorine process for refining gold, by the aid of which many millions sterling of gold have been purified. The late Mr. H. B. Miller based this process for separating silver from gold on the knowledge of the fact that chloride of gold cannot exist at a bright red heat. The tension of dissociation of chloride of gold is high, but the precious metal is not carried forward by the gaseous stream, at least not while chloride of silver is being formed.

The influence of scientific investigation is, however, more evident in that portion of the metallurgical art which deals with the adaptation of metals for use, rather than with their actual extraction from the ores.

Only sixteen years ago Sir Nathaniel Barnaby, then Director of Naval Construction, wrote, "our distrust of steel is so great that the material may be said to be altogether unused by private ship-builders . . . and marine engineers appear to be equally afraid of it." He adds, "the question we have to put to the steel makers is, what are our prospects of obtaining a material which we can use without such delicate manipulation and so much fear and trembling?" All this is changed, for, as Mr. Elgar informs me, in the year ending on June 30 last, no less than 401 ships, of three-quarters of a million gross tonnage, were being built of steel in the United Kingdom.

Why is it, then, that steel has become the material on which we rely for our ships and for our national defence, and of which such a splendid structure as the Forth Bridge is constructed? It is because side by side with great improvement in the quality of certain varieties of steel, which is the result of using the open-hearth process, elaborate researches have shown what is the most suitable mechanical and thermal treatment for the metal; but the adaptation of steel for industrial use is only typical, as the interest in this branch of metallurgy generally appears for the moment to be centred in the question whether metals can, like many metalloids, pass under the application of heat or mechanical stress from a normal state to an allotropic one, or whether metals may even exist in numerous isomeric states.

It is impossible to deal historically with the subject now further than by stating that the belief in more than one "modification" is old and widespread, and was expressed by Paracelsus, who thought that copper "contains in itself its female, which could be isolated so as to give

"two metals" "different in their fusion and malleability," as steel and iron differ. Within the last few years Schützenberger has shown that two modifications of copper can exist, the normal one having a density of 8.95, while that of the allotropic modification is only 8.0, and is, moreover, rapidly attacked by dilute nitric acid which is without action on ordinary copper. It may be added that Lord Rayleigh's plea for the investigation of the simpler chemical reactions has been partly met, in the case of copper, by the experiments conducted by V. H. Veley on the conditions of chemical change between nitric acid and certain metals.

Bergmann, 1781, actually calls iron polymorphous, and says that it plays the part of many metals. "Adeo ut jure dici queat polymorphum ferrum plurimum simul metallorum vices sustinere." Osmond has recently demonstrated the fact that at least two modifications of iron must exist.

Professor Spring, of Liège, has given evidence that in cooling lead tin alloys polymerisation may take place after the alloys have become solid, and it seems to be admitted that the same cause underlies both polymerisation and allotropy. The phenomenon of allotropy is dependent upon the number of the atoms in each molecule, but we are at present far from being able to say what degree of importance is to be attached to the relative distance between the atoms of a metal or to the "position of one and the same atom" in a metallic molecule, whether the metal be alloyed or free, and it must be admitted that in this respect organic chemistry is far in advance of metallurgical chemistry. I cannot, as yet, state what is the atomic grouping in the brilliantly-coloured gold aluminium alloy, AuAl₃, which I have had the good fortune to discover, but in it the gold is probably present in the same state as that in which it occurs in the purple of cassius.

Much valuable information on the important question of allotropy in metals has already been gathered by Pionchon, Ditte, Moissan, Le Chatelier, and Osmond, but reference can only be made to the work of the two latter. Le Chatelier concludes that in metals which do not undergo molecular transformation the electrical resistance increases proportionally to the temperature. The same law holds good for other metals at temperatures above that at which their last change takes place—for example, in the case of nickel above 340°, and in that of iron above 850°.

It is probable that minute quantities of foreign matter which profoundly modify the structure of masses of metal also induce allotropic changes. In the case of the remarkable action of impurities upon pure gold I have suggested that the modifications which are produced may have direct connection with the periodic law of Mendeleeff, and that the causes of the specific variations in the properties of iron and steel may thus be explained. The question is of great industrial importance, especially in the case of iron; and Osmond, whose excellent work I have already brought before the members of this Association in a lecture delivered at Newcastle in 1889, has specially studied the influence upon iron exerted by certain elements. He shows that elements whose atomic volumes are smaller than that of iron delay, during the cooling of a mass of iron from a red heat, the change of the β , or hard variety of iron, to the α , or soft variety. On the other hand, elements whose atomic volumes are greater than that of iron tend to hasten the change of β to α . It is, however, unnecessary to dwell upon this subject, as it was dealt with last year in the Address of the President of the Association.

It may be added that the recent use of nickel-steel for armour plate, and the advocacy of the use of copper-steel for certain purposes, is the industrial justification of my own views as to the influence of the atomic volume of an added element on the mechanical properties of iron, and it is remarkable that the two bodies, silicon and aluminium, the properties of which when in a free state are so totally different, should, nevertheless, when

they are alloyed with iron, affect it in the same way. Silicon and aluminium have almost the same atomic volumes.

The consequences of allotropic changes, which result in alteration of structure, are very great. The case of the tin regimental buttons which fell into a shapeless heap when exposed to the rigorous winter at St. Petersburg is well known. The recent remarkable discovery by Hopkinson of the changes in the density of nickel-steel (containing 22 per cent of nickel), which are produced by cooling to -30° , affords another instance. This variety of steel, after being frozen, is readily magnetisable, although it was not so before; its density, moreover, is permanently reduced by no less than 2 per cent by the exposure to cold, and it is startling to contemplate the effect which would be produced by a visit to the arctic regions of a ship of war built in a temperate climate of ordinary steel, and clad with some three thousand tons of such nickel-steel armour; the shearing which would result from the expansion of the armour by exposure to cold would destroy the ship. Experimental compound armour-plates have been made faced with 25 per cent nickel-steel, but it remains to be seen whether a similar though lessened effect would be produced on the steel containing 5 to 7 per cent of nickel, specially studied by J. Riley, the use of which is warmly advocated for defensive purposes. Further information as to the molecular condition of nickel-steel has within the last few weeks been given by Mercadier, who has shown that alloying iron with 25 per cent of nickel renders the metal isotropic.

The molecular behaviour of alloys is indeed most interesting. W. Spring has shown, in a long series of investigations, that alloys may be formed at the ordinary temperature, provided that minute particles of the constituent metals are submitted to great pressure. W. Hallock has recently given strong evidence in favour of the view that an alloy can be produced from its constituent metals with but slight pressure if the temperature to which the mass is submitted be above the melting-point of the alloy, even though it be far below the melting-point of the most easily fusible constituent. A further instance is thus afforded of the fact that a variation of either temperature or pressure will effect the union of solids. It may be added that B. C. Damien is attempting to determine what variation in the melting-point of alloys is produced by fusing them under a pressure of two hundred atmospheres. Italian physicists are also working on the compressibility of metals, and F. Boggio-Lora has recently established the existence of an interesting relation between the coefficient of cubic compressibility, the specific gravity, and the atomic weight of metals.

Few questions are more important than the measurement of very high temperatures. Within the last few years H. Le Chatelier has given us a thermo-couple of platinum with platinum containing 10 per cent of rhodium, by the aid of which the problem of the measurement of high temperatures has been greatly simplified. A trustworthy pyrometer is now at hand for daily use in works, and the liberality of the Institution of Mechanical Engineers has enabled me to conduct an investigation which has resulted in the adoption of a simple appliance for obtaining, in the form of curves, photographic records of the cooling of masses of metal. A report on the subject has already been submitted to a Committee, of which the Director-General of Ordnance Factories is the Chairman; and Dr. Anderson, to whom I am indebted for valuable assistance and advice, intends to add this new method for obtaining autographic curves of pyrometric measurements to the numerous self-recording appliances used in the Government factories which he controls. It has proved to be easy to ascertain by the aid of this pyrometer what thermal changes take place during the cooling of molten masses of alloys, and it is possible to compare the rate of cooling of a white-hot steel ingot at definite positions situated respectively near its surface

and at its centre, and thus to solve a problem which has hitherto been considered to be beyond the range of ordinary experimental methods. Some of the curves already obtained are of much interest, and will be submitted to the Section. It is probable that the form of the curve which represents the solidification and cooling of a mass of molten metal affords an exceedingly delicate indication as to its purity.

Prof. H. E. Armstrong holds that the molecules of a metal can unite to form complexes with powers of coherence which vary with the presence of impurity. Crookes by a recent beautiful investigation has taught us how electrical evaporation of solid metals may be set up *in vacuo*, and has shown that even an alloy may be decomposed by such means. We may hope that such work will enable us to understand the principles on which the strength of materials depend.

Before leaving the consideration of questions connected with the molecular constitution of metals, I would specially refer to the excellent work of Heycock and Neville, who have extended to certain metals with low melting-points Raoult's investigations on the effect of impurity on the lowering of the freezing-point of solids. With the aid of one of my own students, H. C. Jenkins, I have further extended the experiments by studying the effect of impurity on the freezing-point of gold. Ramsay, by adopting Raoult's vapour-pressure method, has been led to the conclusion that when in solution in mercury the atom of a metal is, as a rule, identical with its molecule. The important research on the liquation of alloys has been extended by E. Matthey to the platinum gold and palladium gold series, in which the manipulation presented many difficulties; and E. J. Ball has studied the cases presented by the antimony-copper-lead series. Dr. Alder Wright has continued his own important investigation upon ternary alloys, and A. P. Laurie has worked on the electromotive force of the copper-zinc and copper-tin and gold-tin series, a field of research which promises fruitful results.

In no direction is advance more marked than in the mechanical testing of metals, in which branch of investigation this country, guided by Kirkaldy, undoubtedly took the leading part, and in connection with which Kennedy and Unwin have established world-wide reputations. I would also specially mention the work which has been carried on at the Government testing works at Berlin under Dr. Wedding, and the elaborate investigations conducted at the Watertown Arsenal, Massachusetts, not to mention the numerous continental testing laboratories directed by such men as Bauschinger, Jenny, and Tetmajer. Perhaps the most important recent work is that described by Prof. Martens, of Berlin, on the influence of heat on the strength of iron.

I might have dwelt at length on all these matters without doing half the service to metallurgy that I hope to render by earnestly pleading for the more extended teaching of the subject throughout the country, and for better laboratories, arranged on the model of engineering laboratories, in which the teaching is conducted with the aid of complete, though small "plant." The Science and Art Department has done great and lasting service by directing that metallurgy shall be taught practically, but much remains to be done. With regard to laboratories in works, which are too often mere sheds, placed, say, behind the boiler-house, when may we hope to rival the German chemical firm which has recently spent £19,000 upon its laboratories, in which research will be vigorously conducted? There is hardly any branch of inorganic chemistry which the metallurgist can afford to neglect, while many branches both of physics and mechanics are of utmost importance to him.

The wide range of study upon which a metallurgical student is rightly expected to enter is leading, it is to be feared, to diminution in the time devoted to analytical chemistry, and this most serious question should be

pressed upon the attention of all who are responsible for the training of our future chemists. There can be no question that sufficient importance is not attached to the estimation of "traces," an analysis being considered to be satisfactory if the constituents found add up to 99.9, although a knowledge as to what elements represent the missing 0.1 may be more useful in affording an explanation of the defects in a material than all the rest of the analysis. This matter is of growing interest to practical men, and may explain their marked preference for chemists who have been trained in works, to those who have been educated in a college laboratory.

The necessity for affording public instruction in mining and metallurgy, with a view to the full development of the mineral wealth of a nation, is well known. The issues at stake are so vast that in this country it was considered desirable to provide a centre of instruction in which the teaching of mining and metallurgy should not be left to private enterprise, or even entrusted to a corporation, but should be under the direct control of the Government. With this end in view the Royal School of Mines was founded in 1851, and has supplied a body of well-trained men who have done excellent service for the country and her colonies. The Government has recently taken a step in advance, and has further recognised the national importance of the teaching of mining and metallurgy by directing that the School of Mines shall be incorporated with the Royal College of Science, which is, I believe, destined to lead the scientific education of the nation.

It is to be feared, if the present prices of metals should be maintained, that as regards metalliferous mining, other than that of iron ores, our country has seen its best days, but the extraordinary mineral wealth of our colonies has recently been admirably described by my colleague, Prof. Le Neve Foster, in the inaugural lecture he delivered early in the present year, on his appointment to the chair so long held by Sir Warrington Smyth (*Engineering*, vol. li., p. 200 *et seq.*). We shall, however, be able to rightly estimate the value of our birthright when the Imperial Institute is opened next year, and the nation will have reason to be grateful to Sir Frederic Abel for the care he is devoting to the development of this great institution, which will become the visible exponent of the splendours of our Indian and colonial resources, as well as a centre of information.

The rapid growth of technical literature renders it unnecessary for a president of a Section to devote his address to recording the progress of the subject he represents. As regards the most important part of our national metallurgy, this has, moreover, been admirably done by successive presidents of the Iron and Steel Institute, but it may have been expected that references would have been made to the main processes which have been adopted since Percy occupied this chair in 1849. I have not done so, because an enumeration of the processes would have been wholly inadequate, and a description of them impossible in the time at my disposal. Nevertheless it may be well to remind the Section of a few of the more prominent additions the art has received in the last half century, and to offer a few statements to show the magnitude on which operations are conducted. As regards iron, in the last twenty-five years the price of steel has been reduced from £55 per ton to £5 per ton, but, after giving the world the inestimable boon of cheap steel by the labours of Bessemer and of Siemens, we were somewhat slow to accept the teaching of experiment as to the best method of treating the new material: on the other hand, Hadfield has brought manganese steel and aluminium steel within the reach of the manufacturer, and J. Riley has done much to develop the use of nickel steel.

In the case of copper, we have mainly contributed to extraordinary development of wet processes for its extraction from poor sulphides, and have met the great

demands for pure metal by the wide adoption of electrolytic processes.

As regards the precious metals this country is well to the front, for Great Britain and her colonies produce about 38 per cent of the gold supply of the world; and it may be well to add, as an indication of the scale on which operations are conducted, that in London alone 1 ton of gold and 5 tons of silver bullion can easily be refined in a day. No pains have been spared in perfecting the method of assay by which the value of gold and silver is ascertained, and during my twenty years' connection with the Royal Mint I have been responsible for the accuracy of the standard fineness of no less than 555 tons of gold coin, of an aggregate value of £70,500,000 sterling. In the case of the platinum industry, we owe its extraordinary development to the skill and enterprise of successive members of the firm of Johnson, Matthey, and Co., who in later years have based their operations upon the results of the investigations of Deville and Debray. Some indication of the value of the material dealt with may be gathered from the statement that 2½ cwts. of platinum may easily be melted in a single charge, and that the firm, in one operation, extracted a mass of palladium valued at £30,000 from gold-platinum ore actually worth more than a million sterling.

I wish it were possible to record the services of those who have advanced metallurgy in connection with this Association, but the limitations of time render it difficult to do more than refer to some honoured names of past presidents of this Section. Michael Faraday, president of this Section in 1837 and 1846, prepared the first specimen of nickel-steel, an alloy which seems to have so promising a future, but we may hardly claim him as a metallurgist; nor should I be justified in referring, in connection with metallurgical research, to my own master, Graham, president of this Section in 1839, and again in 1844, were it not that his experiments on the occlusion of gases by metals have proved to be of such extraordinary practical importance in connection with the metallurgy of iron. Sir Lyon Playfair presided over this Section in 1855, and again in 1859. His work in connection with Bunsen, on the composition of blast-furnace gases, was published in the Report of this Association in 1847, and formed the earliest of a group of researches, amongst which those of Sir Lowthian Bell proved to be of so much importance. The latter was president of this Section in 1889. Sir F. Abel, president of this Section in 1877, rendered enduring service to the Government by his elaborate metallurgical investigations, in connection with materials used for guns and projectiles, as well as for defensive purposes. I will conclude this section of the address by a tribute to the memory of Percy. He may be said to have created the English literature of metallurgy, to have enriched it with the records of his own observations, and to have revived the love of our countrymen for metallurgical investigation. His valuable collection of specimens, made while Professor at the Royal School of Mines, is now appropriately lodged at South Kensington, and will form a lasting memorial of his labours as a teacher. He exerted very noteworthy influence in guiding the public to a just appreciation of the labours of scientific men, and he lived to see an entire change in the tone of the public press in this respect. In the year of Percy's presidency over this Section the *Times* gave only one-tenth of a column to a summary of the results of the last day but one of the Meeting, although the usual discourse delivered on the previous evening had been devoted to a question of great importance, "The Application of Iron to Railway Purposes." Space was, however, found for the interesting statement that the "number of Quakeresses who attended the meetings of the Sections was not a little remarkable." Compare the slender record of the *Times* of 1849 with its careful chronicle of the proceedings at any recent meeting of the Association.

In drawing this address to a close, I would point to the great importance of extending the use of the less known metals. Attention is at present concentrated on the production of aluminium, and reference has already been made to the Cowle's process, in which, as in that of Héroult, the reduction of alumina is effected by carbon, at the very high temperature of the electric arc; while, on the other hand, in the Kleiner and similar processes, the electric current acts less as a source of heat than by decomposing a fluid bath, the aluminium being isolated by electrolytic action; and doubtless, in the immediate future, there will be a rapid increase in the number of metallurgical processes that depend on reactions which are set up by submitting chemical systems to electric stress. Incidental reference should be made to the growing importance of sodium, not only in cheapening the production of aluminium, but as a powerful weapon of research. In 1849, when Percy was President of this Section, magnesium was a curiosity; now its production constitutes a considerable industry. We may confidently expect to see barium and calcium produced on a large scale as soon as their utility has been demonstrated by research. Minerals containing molybdenum are not rare; and the metal could probably be produced as cheaply as tin if a use were to be found for it. The quantities of vanadium and thallium which are available are also far from inconsiderable; but we, as yet, know little of the action of any of these metals when alloyed with others which are in daily use. The field for investigation is vast indeed, for it must be remembered that valuable qualities may be conferred on a mass of metal by a very small quantity of another element. The useful qualities imparted to platinum by iridium are well known. A small quantity of tellurium obliterates the crystalline structure of bismuth; but we have lost an ancient art, which enabled brittle antimony to be cast into useful vessels. Two-tenths per cent of zirconium increases the strength of gold enormously, while the same amount of bismuth reduces the tenacity to a very low point. Chromium, cobalt, tungsten, titanium, cadmium, zirconium, and lithium are already well known in the arts, and the valuable properties which metallic chromium and tungsten confer upon steel are beginning to be generally recognised, as the last Exhibition at Paris abundantly showed; but as isolated metals we know but little of them. Is the development of the rarer metals to be left to other countries? Means for the prosecution of research are forthcoming, and a rich reward awaits the labours of chemists who could bring themselves to divert their attention, for even a brief period, from the investigation of organic compounds, in order to raise alloys from the obscurity in which they are at present left.

It must not be forgotten that metallurgical enterprise rests on (1) scientific knowledge, (2) capital, and (3) labour, and that if the results of industrial operations are to prove remunerative much must depend on the relation of these three elements, though it is difficult to determine accurately their relative importance. A modern ironworks may have an army of ten thousand workmen, and commercial success or failure will depend in no small measure on the method adopted in organising the labour. The relations between capital and labour are of so much interest at the present time, that I do not hesitate to offer a few words on the subject.

Many examples might be borrowed from metallurgical enterprises in this and other countries to show that their nature is often precarious, and that failure is easily induced by what appears to be comparatively slight causes. Capitalists might consequently tend to select Government securities for investment in preference to metallurgical works, and the labouring population would then severely suffer. It is only reasonable, therefore, that if capitalists are exposed to great risks, they should, in

the event of success, receive the greater part of the profits. There is a widespread feeling that the interests of capital and labour must be antagonistic, and as it is impossible to ignore the fact that the conflict between them is giving rise to grave apprehension, it becomes the duty of all who possess influence to strive not merely for peace, but to range themselves on the side of justice and humanity. The great labour question cannot be solved except by assuming as a principle that private ownership must be held inviolable, but it must be admitted that there was a time when capital had become arbitrary and some kind of united action on the part of workmen was needed in self-defence. If, however, we turn to the action of the leaders of trade unions in the recent lamentable strikes, we are presented with a picture which many of us can only view as that of tyranny of the most close and oppressive kind, in which individual freedom cannot even be recognised. There are hundreds of owners of works who long to devote themselves to the true welfare of those they employ, but who can do little against the influence of the professional agitator, and are merely saddened by contact with prejudice and ignorance. I believe the view to be correct that some system by which the workman participates in the profits of enterprise will afford the most hope of putting an end to labour disputes, and we are told that profit-sharing tends to destroy the workmen's sense of social exclusion from the capitalistic board, and contents him by elevating him from the precarious position of a hired labourer. No pains should therefore be spared in perfecting a system of profit sharing.

Pensions for long service are great aids to patience and fidelity, and very much may be hoped from the fact that strenuous efforts are being made by men really competent to lead. The report of the Labour Commission which is now sitting will be looked for with keen interest. Watchful care over the health, interests, and instruction of the employed is exercised by many owners of works; and in this respect the Dowlais works, which are being transplanted into your midst at Cardiff, have long presented a noteworthy example. Workmen must not forget that the choice of their own leaders is in their own hands, and on this the future mainly depends. "We may lay it down as a perpetual law that workmen's associations should be so organised and governed as to furnish the best and most suitable means for attaining what is aimed at, that is to say, for helping each individual member to better his condition to the utmost in body, mind, and property." The words will be found in the Encyclical letter which Pope Leo XIII. has recently issued on the "Condition of Labour." To me it is specially interesting that the Bishop of Rome in his forcible appeal again and again cites the opinion of St. Thomas Aquinas, who was a learned chemist as well as a theologian.

Those of us who realise that "the higher mysteries of being, if penetrable at all by human intellect, require other weapons than those of calculation and experiment," should be fully sensible of our individual responsibility. Seeing that the study of the relations between capital and labour involve the consideration of the complex problems of existence, the solution of which is at present hidden from us, we shall feel with Andrew Lang that "where, as matter of science, we know nothing, we can only utter the message of our temperament." My own leads me to hope that the patriotism of the workmen will prevent them from driving our national industries from these shores, and I would ask those to whom the direction of the metallurgical works of this country is confided, to remember that we have to deal both with metals and with men, and have reason to be grateful to all who extend the boundaries, not only of our knowledge, but also of our sympathy.

A Substitute for Cocks in Vacuum Experiments.—F. de Romilly (*Journal de Physique*).—Mercurial joints are used like those in the Töpler-Hagen mercurial air-pump.

ACTION OF LIGHT UPON DYED COLOURS.*

THE primary object of the work of this Committee is to determine accurately the relative fastness to light of all the various colours at present employed by the dyer of textile fabrics. This is to be attained by exposing to direct sunlight and the ordinary atmospheric influences, patterns of silks, wool, and cotton, specially dyed with the various natural and artificial colouring matters.

The work of purifying these colouring matters, dyeing the patterns, recording the dyed and faded colours of each pattern, &c., &c., must necessarily require much time. Moreover, owing to the very large number of colours to be examined, the long exposure needed to give useful results (one year at least), and the limited capacity of the exposing frame employed, the work will naturally proceed but slowly, and will extend over a period of some years.

During the past year the Secretary of the Committee, has been engaged in collecting samples of the colouring-matters required for the investigation, and in making preliminary exposure experiments with the view of determining the best method of procedure to be adopted.

Having decided to expose the patterns in groups, according to colour, the work of purifying and dyeing with the red colouring-matters has been begun, and is now in progress in accordance with a scheme in the hands of members of the Committee.

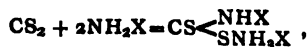
Of the £20 originally granted to the Committee at the last meeting of the Association in Leeds, the sum of £17 10s. has been expended in the purchase of the necessary silk, wool, and cotton material; also an exposing frame, which has been erected at Adel, in the neighbourhood of Leeds.

Particulars of this expenditure have been forwarded by the Chairman of the Committee to the General Treasurer.

NOTE ON THE
PREPARATION OF BENZENOID
DISUBSTITUTED THIOCARBAMIDES FROM
PRIMARY AMINES AND CARBON
DISULPHIDE.

By EMIL A. WERNER, F.C.S., F.I.C.

WHILE no difficulty is experienced in obtaining an almost theoretical yield of a disubstituted thiocarbamide from a paraffinoid amine and carbon disulphide in what, for all practical purposes, may be called a single operation, the same is not the case when dealing with the benzenoid derivatives. The difference is due to the fact that while the formation of a thiocarbamate, according to the equation—



is complete after a few moments in the case of the paraffinoid amines, with the benzenoid derivatives a large proportion of the amine remains unchanged, even after several days' standing, and in presence of a considerable excess of carbon disulphide. Indeed, nothing material is gained by using an excess of the disulphide at the outset, but by adopting the following procedure a very high yield of the thiocarbamide may be obtained within a week and with the minimum amount of the disulphide.

The mixture of amine and carbon disulphide in alcoholic solution, after standing over night, is heated on the water-bath, using a vertical condenser until H_2S ceases to be evolved.

The volume of alcohol need not exceed three times that

* Interim Report of the Committee, consisting of Professor Thorpe, Professor Hummel (Secretary), Dr. Perkin, Professor Russell, Captain Abney, and Professor Stroud; drawn up by the Secretary, British Association, Cardiff Meeting, Section B.

of the amine used, and purified methylated spirits answers admirably, the thiocarbamide produced being sufficiently pure for most purposes without further crystallisation.

The crop of thiocarbamide which separates on cooling is removed, dried, and weighed, while about one-third of the alcohol is distilled off from the mother-liquor; to this latter a quantity of CS_2 is added, depending on the weight of the thiocarbamide obtained, and considering the remainder of the amine to be free. The mixture after remaining over night is again heated on the water-bath until H_2S ceases to be evolved, &c., &c. This is repeated until five or six crops of the thiocarbamide have been obtained. The preparation is no doubt somewhat tedious, but it requires little attention, and the reward is an almost theoretical yield of the product.

Thus in the course of a recent investigation, necessitating the preparation of some benzenoid thiocarbamide, the yields obtained were as follows:—

1. 64.2 grms. orthotoluidine yielded 69.32 grms. di-orthotolylthiocarbamide = 90.26 per cent of theoretical.
2. 85.6 grms. paratoluidine yielded 96 grms. diparatolylthiocarbamide = 93.7 per cent of theoretical.

3. 28 grms. metatoluidine yielded 32.37 grms. of dimetatolylthiocarbamide = 94.90 per cent of theoretical.

4. 72.6 grms. metaxylidine yielded 82.95 grms. of dimetaxylthiocarbamide = 97.32 per cent of theoretical.

The author's method for the preparation of the benzenoid "mustard oils" (*Trans. Chem. Soc.*, June, 1891), taken in conjunction with the above yields, renders the conversion of an aromatic amine into its corresponding thiocarbimide an operation, which follows closely at the heels of theory.

University Laboratory,
Trinity College, Dublin.

ABSORPTION-SPECTRUM ANALYSIS OF HIGHLY DILUTE SOLUTIONS.*

By O. KNOBLAUCH.

THE author summarises his results as follows:—

1. Beer's law of absorption (*Poggendorff's Ann.*, ci., p. 248) is valid for the solutions of many salts within a very wide range of concentration. It was found confirmed even when the gaseous pressure corresponding to the proportion of salt in the solution rose from $\frac{1}{1000000}$ atmosphere to 25 atmospheres. The seeming deviations from the law may be traced to physical or chemical changes of the solutions.

2. The differences in the absorption-spectrum of the salts of one metal with different acids or of one acid with different metals remain permanent.

3. The two inferences drawn from the dissociation hypothesis of Prof. Arrhenius on absorption spectra are not found to be confirmed by the observations. In the eosine salts the dilution was so great that 1 grm. of the dissolved body was contained in not less than millions of litres, so that, according to the hypothesis, a complete dissociation of the dissolved molecules must be assumed. According to the second inference, the various eosine salts should have the same absorption-spectrum. This, however, was not the case, but even in dilute solutions the absorption band in the salts of the light metals has a different position from those of the heavy metals. This experimental fact disagrees with the hypothesis.

The two inferences referred to are:—

1. The absorption-spectrum of the concentrated slightly dissociated solution of a body must be different from that of the highly dilute and almost completely dissociated solution; since, in the former, the absorption is produced chiefly by the non-dissociated molecules, but in the latter by the dissociated molecules.

2. At a sufficient dilution at which the limit-condition of dissociation has been reached, the absorption-spectrum of different salts of the same coloured metal (or of the same coloured acid) becomes alike, always supposing that in the dissociated solutions of the salts in question the absorption is produced by the same ion.

CONTRIBUTIONS TO THE CHEMISTRY OF ERBIUM AND DIDYMIUM.*

By GERHARD KRÜSS.

(Concluded from p. 101).

Behaviour of the Earths with Potassium Oxalate (K Bröckelmann and G. Krüss).—A further distinction between the salts of erbium and didymium consists in the behaviour of the oxalates with potassium oxalate. According to Höglund, erbium oxalate behaves with potassium oxalate like the corresponding yttrium salt, which, according to Cleve, dissolves in a hot concentrated solution of potassium oxalate with formation of a soluble double potassium salt. According to the observations of the authors, didymium is not capable of forming such a readily soluble double potassium salt, therefore the following experiment was performed:—

Two hundred grms. didymium and yttrium nitrates were mixed with the concentrated solution of 1 kilo. potassium oxalate, and digested in heat. The precipitate filtered off after twenty-four hours was dried and ignited. The earth contained in the residue was converted into a neutral nitrate, and showed in its absorption spectrum only a slight indication of the erbium lines, e.g., at $\lambda=653.9$, and, according to its spectrum, consisted chiefly of didymium and holmium.

The double oxalates which remained in solution, on digestion in potassium oxalate, could not be decomposed by ammonia, whence their solution was first evaporated to dryness with concentrated nitric acid. A micro-crystalline powder was separated out, which, after filtration, solution in much water, precipitation of a voluminous hydroxide with ammonia, and re-solution of the precipitate in nitric acid, yielded a nitrate almost entirely free from didymium.

In order to ascertain whether, besides the erbium earths, colourless earths had passed into the potassium oxalate solution, the molecular weight of the earth thus obtained was determined.

A conversion of oxide into an anhydrous sulphate gave almost the same value as the ignition of a weighed quantity of dry oxalate and its conversion into oxide.

As a mean there was formed $R=107.1$, whence it follows that in the potassium oxalate solution of the mixed

oxalates there was present, along with $\text{Er}=166$, a considerable quantity of yttrium (atomic weight = about 89), or possibly of scandium.

Some further experiments were made to test the behaviour of mixtures of rare earths with potassium oxalate, and to this end was used an earthy mixture obtained from keilhaute, and not further fractionated. A nitrate solution of such earths was first precipitated with oxalic acid, the oxalates were washed, and boiled for some hours with a concentrated solution of potassium oxalate. A considerable part of the precipitate passed into solution, so that all the lines were present in the absorption spectrum of the solution as in that of the precipitate. If the oxalates are not boiled for some hours with potassium oxalate, but digested only at the common temperature of a room, an erbium passes into solution, the absorption spectrum of which shows no trace of the Dy lines at $\lambda=579.2$ and 575.4 .

* From the *Annalen der Physik und Chemie*, New Series, vol. xliii

* *Liebig's Annalen*.

The following experiment proves that along with erbium, in addition to yttrium, other colourless earths pass into solution on the digestion of the oxalate with potassium oxalate. The concentrated solution of potassium salt, with which the oxalates were digested for some hours, was evaporated to dryness, the residue ignited and extracted with water. Besides the potassium carbonate obtained a part of the earths was now soluble in water, for the solution yielded a precipitate with ammonia.

The hydroxide, after being well washed, yielded a nitrate solution, which in its most concentrated state, and in a stratum of several centimetres in thickness, showed only one line, i. e., $\text{Er}\beta$ at $\lambda = 523.1$. The line was faint, so that along with a little erbium a colourless earth was chiefly present in the nitrate in question. To obtain a decision a determination of the molecular weight was undertaken. To this end the earth present was most carefully purified, small portions of the metals precipitable by hydrogen sulphide being first removed from the solution of the nitrate. The filtrate of the precipitate was boiled and precipitated with ammonia, the hydroxide thrown down was dissolved in nitric acid, the earth was again precipitated with oxalic acid from an acid solution, and the oxalate was converted by ignition into an oxide almost perfectly white; its colour was very slightly altered on ignition in a current of hydrogen, and it consisted of a colourless earth accompanied by traces of erbia and perhaps also of didymia.

On analysis it was found that 0.2166 grm. of the oxide yielded 0.4727 grm. of anhydrous sulphate, showing a $\text{R} = 77.5$. The small quantity of colourless earth obtained in this simple manner from keilhaute consists therefore chiefly of scandia, since only the presence of this oxide can reduce the atomic weight below the value of yttrium. By a treatment of the earthy oxalates with potassium oxalate it is therefore possible, by a single operation, to eliminate erbium, and many colourless earths, from didymium, and under the above experimental conditions quickly to obtain a scandium material.

Behaviour of the Neutral Solution of the Nitrates of the Rare Earths with Alcohol (K. Bröckelmann).—Concerning a differing solubility of the earthy nitrates in alcohol there have been hitherto no definite communications. It must therefore be remarked that the neutral nitrate solution of the (nearly) colourless earth obtained by the potassium oxalate process as just described, and

having the low atomic weight ($\text{R} = 77.5$), can be completely precipitated by the addition of an excess of alcohol. This is the more striking as an ordinary nitric solution of the rare earths—e.g., such as they are directly obtained from the gadolinites—is not precipitable by alcohol.

Further experiments were therefore made, in the first place with a didymium material obtained by the methods above described, and having the mean atomic weight. This didymium could not be resolved into portions having different spectra, either by fractionated crystallisation or by the decomposition of the nitrates by heat.

The faintly acid solution of this didymium was evaporated to dryness on the water-bath, and taken up in a little water, so as to obtain a neutral solution of nitrate as concentrated as possible. This liquid was mixed with a large excess of absolute alcohol, the whitish precipitate was filtered off and washed with alcohol. The nitrates insoluble in alcohol were dissolved in a little water, again precipitated with alcohol, and this treatment was repeated three times. A portion each time passed into solution, and the earth obtained after this thrice-repeated alcoholic precipitation as an insoluble nitrate was submitted to several determinations of its molecular weight.

The earth possesses the properties of didymium oxide of being reducible in a current of hydrogen to a lower oxide. The oxide was light brown, the sub-oxide white: 0.4521 grm. oxide yielded on ignition 0.4491 grm. sub-

oxide, which corresponds to a decrease of oxygen of 0.66 per cent. Hence it was seen that it was not a didymium in the ordinary sense of the word (Cleve's and Brauner's didymium), for those savants found a greater difference in the percentage of oxygen in the two stages of oxidation of didymium. The same holds good with cerium. It was also evident, from the relatively faint absorption-spectrum of the nitrates precipitable by alcohol, that we have in these precipitates a mixture of colourless earth with such as produce absorption spectra, and that therefore, by treating the nitrates with alcohol, one more colourless earth could be removed from ordinary didymium.

In order to obtain a clue to the nature of this earth, the nitrates insoluble in alcohol were dissolved in water, carefully purified for determination, converted into oxalate oxide, and then, by ignition in a current of hydrogen, into sub-oxide. Weighed quantities were converted into anhydrous sulphate, and on the analysis of different products the following results were obtained:—

Grammes of Suboxide taken.	Grammes of Anhydrous Sulphate found.	Atomic Weight calcu- lated for a R.
0.2342	0.4417	111.4
0.0861	0.1625	111.9
0.2594	0.4928	111.5

Mean 111.6

The values obtained were considerably lower than the mean atomic weight of didymium: 144–145.

Hence, especially as the spectroscopic examination pointed to a mixture of didymium with a colourless earth obtained by treating the ordinary didymium nitrate with alcohol, yttrium and perhaps also scandium have been removed from the didymium. Further, the material insoluble in alcohol was purified by frequently repeated treatment of the neutral nitrate with alcohol. The thrice precipitated material with the above mean atomic weight of 111.6, after a fourth similar treatment, showed almost

the same atomic weight, $\text{R} = 111.28$.

Still the above behaviour of the didymium nitrate is interesting, and should be taken into account in the preparation of pure didymium material. It should be examined whether, on treating the concentrated neutral solution of nitrate with alcohol, an earth of lower atomic weight may not be separated from didymium oxide.

The above research on the elements of the yttrium and cerium group affords some contributions towards the mutual separation of these elements from each other. It is at the same time evident, from the experiments cited, how sparingly characteristic are the properties of the several rare earths from an analytical point of view, and that difficulties have to be encountered in the separation of these oxides. It is therefore questionable whether many of the rare elements actually possess the atomic weights which have been hitherto attributed to them. In a succeeding memoir the observations made in this respect upon erbium will be communicated.

ON THE DETERMINATION OF NITRATES IN WATER.*

By ALLEN HAZEN and HARRY W. CLARK.

I. Phenosulphonic Acid Process.

THE accurate determination of nitrates, in large numbers of samples of water, has presented considerable difficulty. A few years ago the phenosulphonic acid process (Grandval and Lajoux, C. R., July 6, 1885) was selected, as being on the whole the most satisfactory, and with it we have made several thousand determinations.

The process consists, essentially, of evaporating a measured portion of water to dryness, and treating the residue with a solution of phenol in sulphuric acid, a portion of which the nitric acid liberated converts into nitrophenols, which, when made alkaline, are strongly yellow. The colour so produced is compared with that obtained in a similar way from known quantities of potassium nitrate.

The accuracy of the results was greatly increased by adding sodium carbonate to prevent the loss of nitric acid during evaporation, and by decolourising yellow surface waters by alumina.

The best results were obtained with about 1 c.c. of a 5 per cent solution of strictly pure phenol in sulphuric acid nearly free from water, added to the dry residue, and without warming. Caustic soda or potash was substituted for ammonia, in neutralisation, to avoid the fumes of the latter.

An attempt was made to use standards made from pure picric acid, but to our surprise their colour was only a third as deep as that of standards made by treating potassium nitrate with phenolsulphonic acid. Other nitrophenols were then tried, but none matched the standards perfectly. It was possible to match particular standards by mixing different nitro-compounds, but for other standards different mixtures were required. It was obvious that in our standards, prepared from potassium nitrate, we were not dealing with a pure compound, but with a mixture of varying proportions of different nitrophenols, and, as the different compounds are by no means of the same colour for equal contents of nitrogen, variations in the proportions of the different compounds formed gave rise to very serious errors. The principal products are usually ortho- and para-monomonitrophenol in varying proportions.

The following table shows the strength of solutions of some of the nitrophenols which give colours equal to those of average standards prepared from potassium nitrate, when seen through a depth of 8 inches of solution:—

Comparison of Solutions of Nitrophenols.

(Parts per Million Nitrogen in a Depth of 8 Inches.)

Standard from KNO ₃ .	Orthomono-nitrophenol.	Paramono-nitrophenol.	Dinitrophenol.	Trinitrophenol.
0.02	0.022	0.014	0.04	0.06
0.04	0.040	0.026	0.08	0.14
0.06	0.060	0.044	0.12	0.22
0.08	0.076	0.064	0.18	0.32
0.10	0.090	0.08	0.23	0.42
0.12	0.110	0.12	0.31	0.60
0.14	0.124	0.16	0.38	0.80
0.20	0.16	0.36	0.60	1.40
0.40	0.22	1.80	1.40	3.00
0.60	0.30	7.00	3.00	6.00
1.00	0.38	12.00	6.00	9.00
1.40	0.46			
4.00	1.00			
10.00	2.00			

We have not been successful in so controlling the reaction as to get a constant product, or in finding a substituted phenol with which there can be only a single nitro-compound, and which is at the same time sufficiently soluble in water, and otherwise adapted to the process. If such a compound could be found the accuracy of the process might be greatly increased.

The presence of chlorine lowers the result, often seriously. The error increases with the ratio of chlorine to nitrate, but is not proportional to it. Numerous experiments do not show sufficient regularity to allow even an approximate estimate of the error in particular cases. The results of this process upon a hundred and fifty ground waters averaged 11 per cent lower than the results obtained by reduction by the aluminum process, with the precautions to be described, and it is believed that this

represents approximately the average error due to chlorine in these particular cases. In some instances we have removed the chlorine with silver sulphate, and obtained higher results; but even then the results are liable to the errors described above.

This process, with proper precautions, gives results usually too low, and often much too low, and, while it may be useful in some cases, we have been unable to obtain results of the desired accuracy.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1891.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolitan Water Act, 1871.

London, August 5th, 1891.

SIR,—We submit herewith the results of our analyses of the 186 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 186 samples examined, the whole were found to be clear, bright, and efficiently filtered.

The character of the water supply to the Metropolitan during the month of July was in all respects satisfactory, the proportion of organic matter present in the water being below even the exceptionally small amount recorded in the month of May.

There was not found to be any appreciable difference in character between the water distributed by the five Companies taking their supply from the Thames, and the water distributed by the East London Company, who take their supply from the Lea; but what slight difference was found to exist was in favour of the Lea-derived water, as shown in the following Table:—

	Ratio of brown to blue tint. Means.	Oxygen required for oxidation. Means.	Organic carbon per 100,000 Means.	Organic carbon per 200,000 Maxima.
<i>Thames supply:—</i>				
January ..	13.0 : 20	0.051	0.147	0.209
February ..				
March ..				
April ..				
May ..	9.6 : 20	0.042	0.136	0.150
July ..	8.9 : 20	0.046	0.121	0.143
<i>Lea supply:—</i>				
July ..	8.2 : 20	0.041	0.119	0.124

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 112).

XXIII.—Gold.

1. Stannous chloride produces in the solution of gold a red turbidity which is very well suited for microscopical recognition. It is best to place the specimen and the reagent near each other, and allow the drops to flow together. There then appears a rather sharply marked red streak at the point of contact. The limit of the reaction is 0.002 m.grm. Au.

2. Thallous sulphate produces in solutions which contain at least 0.17 gold the crystallisation of long, yellow needles of thallous aurochloride. The needles may exceed the length of 1000 micro. The limit of the reaction is 0.01 m.grm. Au.

The solution is concentrated by evaporation as far as possible, partly in order to expel nitric acid, and a granule of thallous sulphate is introduced into the drop when cold. The reaction sets in at once and is localised around the reagent. The application of heat readily occasions a reduction of gold, and the separation of hexagonal leaflets of thallic chloride.

3. Ammonium sulphocyanide produces in solution of gold a red powdery precipitate, which, in an excess of the reagent, is converted into pale red, woolly rosettes. A larger excess dissolves if heated to a colourless liquid, which precipitates salts of zinc and cobalt in a manner similar to ammonium-mercuric sulphocyanide. Zinc-gold sulphocyanide is lemon-yellow, cobalt-gold sulphocyanide a blue green. Their form agrees with the form of the corresponding double salts of mercuric sulphocyanide. Together they form sea-green mixed crystals. It is not yet certain whether there may be formed mixed crystals containing mercury and gold.

XXIV.—Platinum.

(a) *Platinous Chloride*.—1. Precipitation as cuprammonium-chloroplatinite (salt of Millon and Commaille). If a solution of potassium chloroplatinite is mixed with a little copper sulphate, rather much sal-ammoniac, and an excess of ammonia, violet needles are quickly deposited, which, in solutions with 0.1 per cent potassium chloroplatinite become 200 micro. in length, and are deposited in a recognisable form when they contain 0.01 per cent. Limit of the reaction 0.00006 m.grm. Pt.

(b) *Platinic Chloride*.—1. Potassium chloride yields well-developed yellow octahedra of 10–50 micro. In solutions containing less than 0.1 per cent platinum chloride, potassium chloride acts too slowly; very dilute solutions must be evaporated to dryness in order to obtain crystals of potassium-platinum chloride. If alkaline salts are present in considerable quantity, this process is not satisfactory, and we are compelled to have recourse to the reactions 2 or 3. Limit of the reaction with potassium chloride 0.0006 m.grm. Pt.

2. Rubidium chloride precipitates almost instantaneously solutions containing 0.1 per cent of platinum chloride. The crystals of rubidium chloroplatinate are about one-third of the size of those of the potassium salt.

Cæsium chloride reacts instantaneously in solutions containing 0.03 per cent of platinum chloride. The crystals have then a diameter of 2 micro. Limit of the reaction 0.0002 m.grm. Pt.

3. Thallous sulphate reacts distinctly with platinic chloride diluted to 1:20,000. The crystals are very small, and from concentrated solutions there is precipitated a yellow dust. Confusion with chloroiridate is excluded, as iridic chloride is reduced by thallous sulphate. The limit of the reaction is 0.000004 m.grm. Pt.

XXV.—Palladium.

1. Potassium iodide throws down a brown, flocculent precipitate, which dissolves with a reddish brown colour in an excess of the reagent.

With ammonia palladio-iodide gives orange-red needles and a colourless solution, from which palladammonium iodide is deposited in pale yellow, rectangular rosettes of 20–30 micro. An excess of potassium iodide interferes. As a corrective evaporation with hydrochloric acid may be tried. Limit of the reaction 0.0001 m.grm. Pd.

2. Ammonium sulphocyanide produces a brown colouration in solutions of palladium. An addition of thallous sulphate then produces a strong, yellowish brown precipitate, the solution of which in hot water deposits rectangular rosettes of 100 micro, which grow to iridescent leaflets. From very dilute solutions there are obtained rectangular prisms and crosses of 30 micro. The reaction is still produced when the palladium nitrate is diluted with 5000 parts of water. Its limit is at 0.00007 m.grm. Pd.

XXVI.—Iridium.

1. Rubidium chloride instantly precipitates a solution of iridium sal-ammoniac (ammonium chloriridate) in 300 parts of water; in a solution with 1500 parts of water there appears in some minutes a vermilion-red precipitate consisting of octahedra of 10 micro.

Cæsium chloride throws down at the same dilution almost instantly very small but well-developed red octahedra. The limit of the reaction is 0.0003 m.grm. Ir.

XXVII.—Rhodium.

1. Potassium nitrite throws down from acid and ammoniacal solutions of rhodium yellow cubes of 2–4 micro. The precipitate adheres to the glass like potassium-cobalt nitrite. The liquid may be diluted with 10,000 parts of water. The limit lies at 0.00009 m.grm. R.

XXVIII.—Ruthenium.

1. Cæsium chloride produces in solutions of ruthenium in aqua regia a reddish brown, finely granular precipitate, soluble in hot water, but being re-deposited unchanged from this solution. Limit of reaction 0.0008 m.grm. Ru.

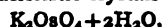
2. Potassium sulphocyanide colours acid ruthenium solutions a violet-red. If the colour does not appear at once the liquid is concentrated by a gentle heat, and the margin of the specimen drop is carefully watched. The reaction is not sensitive; its limit is 0.0012 m.grm. Ru. It is useless in presence of iron, cobalt, platinum, and palladium. A good micro-chemical reaction for ruthenium has yet to be discovered.

XXIX.—Osmium.

1. Cæsium chloride produces in solutions of osmic acid in hydrochloric acid a whitish precipitate consisting of greenish yellow octahedra of 10–30 micro. The limit of the reaction is 0.0001 m.grm. Os.

2. Ammonium chloride, added in excess to solutions of potassium osmite, separates yellow rods (40–70 micro.), and dendrites of osmiotetrammonium-dichloride. The limit of the reaction is 0.0005 m.grm. Os.

In less dilute solutions the reduction to potassium osmite (with potassa-lye and potassium nitrite or alcohol) yields characteristic crystals of osmite—



which separates out in fine, violet-red octahedra, of 50 micro.

XXX.—Tin.

(a) *Stannous Chloride*.—Gold chloride produces in solutions containing stannous chloride a flocculent red precipitate, or in very dilute solutions a red turbidity. (See Gold 1). Limit of the reaction 0.00007 m.grm. Sn.

2. Mercuric chloride is reduced by stannous salts to insoluble mercuric chloride, even in very dilute solutions. (Compare Mercury b 2). Limit 0.00007 m.grm. Sn.

* Zeit. Anal. Chemie.

3. Oxalic acid is recommended by Haushofer as a reagent for stannous salts. The use of potassium oxalate increases the sensitiveness, which, however, is far below 1 and 2. The crystals are mostly imperfect, H-shaped, and polarise strongly. Limit of the reaction 0.001 m.grm. Sn.

In all these reactions it must be remembered that arsenic acid forms with tin a very stable, insoluble compound, which is not readily decomposed by hydrochloric acid.

(b) *Stannic Chloride*.—1. Cæsium chloride precipitates from solutions of stannic chloride colourless octahedra of Cs_2SnCl_6 . (Compare Cæsium 1). The precipitation is but little interfered with by hydrochloric acid. An addition of potassium iodide slightly increases the sensitiveness and colours the crystals yellow. The limit of this convenient and trustworthy reaction is 0.00045 m.grm. Sn.

2. The changes of form which stannic chloride occasions in the oxalates of barium and strontium have been mentioned under Strontium 4. In acid liquids the greatest sensitiveness is reached with strontium salts. Limit of the reaction 0.0002 m.grm. Sn.

Meta-stannic acid must be fused with alkali or reduced with magnesium. It is dissolved in hydrochloric acid and treated in the first case according to *b* 1, in the second according to *a* 1 or 2.

XXXI.—Titanium.

1. Potassium salts precipitate from solutions of titanium dioxide in hydrofluoric acid, potassium fluotitanate, in pale rectangular figures, rhombs, octagons, and long hexagons of 60–90 micro. The precipitation is tedious, and the limit is 0.06 m.grm. Ti.

If rutile is fused with potassium fluoride at a bright red heat, and the melt is dissolved in hot water, needles are deposited which might be taken for fluotantalate. They dissolve in hydrochloric acid, and the solution yields the tabular crystals just mentioned.

2. Rubidium chloride precipitates fluoriferous solutions of titanic acid more readily than potassium chloride. Solutions containing 0.2 per cent of titanium dioxide give within 2 minutes crystals of rubidium fluotitanate. They measure 15–40 micro., and otherwise resemble those of the potassium salt. Cæsium chloride instantly precipitates tablets of 8–12 micro. Limit of the reaction 0.001 m.grm. Ti.

Insoluble titanic acid may be fused with alkali, the melt extracted with hot water, and the residue dissolved by heating with concentrated hydrochloric acid. It is preferable to fuse with sodium fluoride and dissolve the melt in dilute hydrochloric acid.

XXXII.—Zirconium.

1. Potassium bioxalate precipitates from solutions of zirconium sulphate (down to a proportion of 0.01 per cent of the sulphate) colourless pyramids of 20–60 micro. (probably tetragonal), similar to strontium oxalate, but more readily soluble in hydrochloric acid. The limit of the reaction is 0.00006 m.grm. Zr.

Oxalic acid gives a precipitate only when diluted down to 200 parts. Titanium solutions are not precipitated by oxalic acid and bioxalates; neutral oxalate precipitates small rods. Zircon is best opened up by means of sodium fluoride like titanium, and evaporating down with sulphuric acid.

2. Rubidium chloride occasions in solutions of zirconium sulphate or chloride, mixed with hydrochloric acid and ammonium fluoride, a separation of colourless octahedra, which measure 30–60 micro. The rubidium chloride yields the same strongly refractive crystals in the hydrochloric solution of a melt of zircon and sodium fluoride. Cæsium chloride gives similar, though smaller, crystals. The limit of the reaction is 0.0005 m.grm. Zr.

XXXIII.—Thorium.

1. Heating to close upon 100°, precipitates from solutions of thorium sulphate, if not too dilute, fine needles of 70–100 micro. of the sparingly soluble salt with 3 mols. of water. The limit of the reaction is 0.03 m.grm. Th.

Upon one end of the port-object is laid a covering-glass, upon which is laid the specimen drop. It is heated to incipient ebullition, the marginal crust is broken, and the covering-glass is pushed upon the cold half of the port-object. This is a rapid and trustworthy reaction for quantities of thorium which are not too minute. Confusion with the sulphates of the cerite metals (especially lanthanum) and the needles of gypsum remains excluded if we test further with ammonia and with ammonium carbonate (see 3).

2. Oxalic acid produces a white powdery precipitate, sparingly soluble in hydrochloric acid, more readily soluble in ammonia and ammonium carbonate. Very dilute solutions yield a finely crystalline oxalate, especially rods of 4 micro. The limit of the reaction is 0.0001 m.grm. Th.

3. Thallous sulphate occasions in ammoniacal solutions of thorium the separation of sharp colourless rhombs and flat rhombic pyramids of 30–40 micro. Very dilute solutions yield during evaporation along the margin rhombs of 4–10 micro. The limit of the reaction is 0.00005 m.grm. Th.

The solution to be examined is precipitated with ammonium carbonate, adding an excess, and the solution is accelerated by adding ammonia. A granule of thallous sulphate sets up the reaction above mentioned. From uranium thorium is distinguished by reactions 1 and 2.

(To be continued).

NOTICES OF BOOKS.

Water Works' Statistics, 1891. Edited by C. W. HASTINGS. London: Hazell, Watson, and Viney.

THE usefulness of this compilation is still somewhat limited by the neglect or refusal of local bodies to supply information. The town of Aylesbury still maintains silence, though it has assuredly no reason to be ashamed of its water-supply. Stafford, Stowmarket, and Stockport likewise vouchsafe no information as far as we can trace, but many towns whose names begin with R and S are, by some accident, placed in unalphabetical order.

The heading "Source of Supply" is still open to amendment. Ambleside sensibly says that its water comes from the "green slate," whilst Bacup gives as its source "sandstone and peat." But, on the other hand, some towns say merely that they derive their water from "wells," or from "gathering grounds," without any clue to the character of the formation. A few places still assign "gravitation" as the source of their supply, leaving its origin an open question.

The information concerning the quality of the water is often lacking in precision. Many towns call their water simply "good," "soft," or "hard," as the case may be, whilst others give the degree of hardness. The local death rates are omitted in a number of cases. We can find little definite relation between the mortality of the towns and the character of the water-supply as hard or soft. So many other factors, however, intervene in determining the death rate of a town, that the omission is of the less importance.

The statistics of the water-supplies in Scotland, Wales, and Ireland are given very promiscuously, and mixed up with such localities as Shanghai, St. Petersburg, and Monte Video.

The daily consumption per head is a feature of no little importance both to sanitarians and to all persons interested in the utilisation of sewage. But a very large proportion of towns have vouchsafed no information.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 6, August 10, 1891.

This issue does not contain any chemical matter.

Vol. cxiii., No. 7, August 17, 1891.

A New Blowpipe for Mineral Oils.—M. Paquelin.—This apparatus comprises three essential parts: a blowpipe—properly speaking—a carburettor, and a double-action blast. The blowpipe is formed of a single tube, like the mouth blowpipe used by jewellers. The jet has this characteristic, that it emits two kinds of flames: a central flame with a very narrow point, and small lateral flames in the form of petals. The carburettor serves for three purposes: (1) to mix air and the vapours of the oil in proportions regulated at will; (2) to exhaust the combustible of all its useful elements; and (3) to regulate the length of the flame at pleasure. These results are obtained by means of two cocks and a saturator. One of the cocks is of a special structure; the other is of the ordinary make.

New Researches on the Solar Atmosphere.—H. Deslandres.—The author has studied the atmosphere of the sun in a part of its radiation not yet explored. He has obtained the permanent feeble ray, rather more refrangible than H, and indicated in Young's list with the note "element unknown." He has identified this ray with a hydrogen ray. In the invisible ultra-violet portion he has recognised two new permanent rays which correspond to the two first rays of hydrogen of the stellar series of Dr. Huggins. The most striking result is the marked predominance of the rays attributed to calcium; the corresponding rays rise higher than hydrogen, which contradicts our received ideas on the composition of the solar atmosphere.

Mechanical Determination of the Catenation of the Atoms of Carbon in Organic Compounds.—G. Hinrichs.—The atoms of carbon do not as generally represented follow a single right line.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. v., No. 11.

On the Second Principle of Thermodynamics and its Application to Chemical Phenomena.—H. Le Chatelier.—To render Carnot's principle applicable to chemical phenomena it is merely necessary to suppress every restriction on the nature of the equilibrium, the re-establishment of which is in question, which is tantamount to striking out the term "caloric" in Carnot's enunciation. We then read, "Wherever there may be re-establishment of equilibrium there may be production of motive power, and reciprocally wherever such power is consumed it is possible to occasion a breach of equilibrium." This leads us, without calculation, to two chemical laws which have long been known—the law of the triple point and the law of the maximum stability of the various states of a body. From the same principle there may be deduced by a very simple calculation the two laws of iso-dissociation and of the direction of chemical movement. The same method of calculation is applicable to the quantity of available energy furnished by the return of a chemical system towards its state of equilibrium.

On the Allotropic Transformations of Metals.—H. Le Chatelier.—From the author's experiments it results that metals, as regards their molecular transformation, behave exactly like the other bodies studied in chemistry—that is, the transformations either take place abruptly,

the metal behaving in that case like all crystalline bodies (definite compounds or isomorphous mixtures), or progressively in the case of alloys which behave like amorphous mixtures (solutions or glasses). The existence of these two states in metals is shown in many cases by a simple inspection of the fracture. The extreme variability of the mechanical properties of metals is explained without the intervention of any special isomerism by remarking that they depend not only on the chemical state of the metal, but on the form and the dimensions of the crystals or granules of metal which are in juxtaposition, and on the manner of distribution of the impurities.

On Some Combinations of Pyridine.—Raoul Varet.—An account of the preparation and properties of pyridine bromocadmiate, bromozincate, bromonickelate, bromocuprate, iodocuprite, cyanocuprite, cyanomercurate, cyanoargentate, argentoiodide, argentobromide, and argento-chloride.

Formation of Dimethylacrylic Acid in the Preparation of the Amido-Acids of Isovaleric Acid.—E. Duvillier.—The relatively small product of amido-acids obtained on causing ammonia and the compound ammonias to react upon bromoisovaleric acid, is due to the simultaneous formation of a notable quantity of dimethylacrylic acid.

Researches on the Influence of Wines upon Pepsic Digestion.—L. Hugouenq.—Without dwelling upon the known action of alcohol, which has been well studied by Petit, and upon that of cream of tartar, the novel results arrived at in the author's researches are the following:—1. All wines, without exception, interfere with the action of pepsine—those richest in alcohol, cream of tartar, and colouring-matter being most injurious, as it was easy to foresee. 2. Among the elements of natural wine the colouring-matters act in concert with the alcohol and the cream of tartar to retard or arrest pepsic digestion. 3. The acidity of normal wines is unable to excite the action of pepsine; in most cases it does not appear to assist. 4. Among the colouring-matters introduced fraudulently into wines, methylene blue, azoflavine, solid blue, and especially magenta, interfere with pepsic digestion. The vegetable colours, black mallows, elderberries, and maki, like conoline exert an injurious action. 5. Plastering, by removing a part of the cream of tartar, eliminates an element of natural wines which retards the action of pepsine *in vitro*. Digestion is more rapid in presence of plastered wines than of natural wines, but the advantage which plastered wines have in this respect does not conceal their other disadvantages.

On the Use of Metaphenylenediamine to Detect Active Oxygen.—P. Cazeneuve.—The author makes a solution of 1 per cent of the hydrochlorate of this base in alcohol at 93 per cent. Ten drops of ammonia are added to the solution. If this reagent is exposed to the air, or exposed to a current of oxygen for many hours, it takes a slightly greenish blue tint. A few drops of oxygenated water added to 10 c.c. of the reagent colour it intensely blue in a few minutes in the cold.

On a Violet Colouring-Matter Derived from Morphine. On the Formula of Pseudomorphine.—P. Cazeneuve.—The author has caused paranitrosodimethylaniline to react upon morphine. He obtains a violet colouring-matter which is neither an indophenol nor a safranin, but which may enter the group of the azines or the indamines, or constitute the type of a special group of colouring-matters. The pure colouring-matter has the composition $N \begin{smallmatrix} C_6H_4 \cdot N(CH_3)_2 \\ C_{17}H_{19}NO_4 \end{smallmatrix}$. It is amorphous, with a bronze reflection. It is to a certain extent soluble in water, from which it is precipitated by common salt. It is very soluble in methylic, ethylic, and amylic alcohols, in which it displays very decided dichroism. In amylic alcohol especially it is red by reflected, and violet by transmitted, light. The aqueous solution, if poured upon

strong sulphuric acid, gives, like the safranines, a green zone, then blue, and then violet. It dyes wool, silk, and gun-cotton in a direct manner. The shade produced on silk is brilliant, but it does not withstand light. This morphine violet is the first true colouring-matter obtained from a natural alkaloid.

On the Hydrazonic Derivatives of β -Naphthoquinone.—E. Noelting and E. Grandmougin.—The colouring-matters derived from the hydrazone of β -naphthoquinone, and especially its sulphonic derivative, which is an isomer of the oranges I. and II. of commerce, have all the characters of the azo-compounds. Their study leads the authors to conclude that the hydrazone of β -naphthoquinone is an azo-derivative, and not a hydrazone. This sulphonic derivative is a true ponceau, which is quite distinct from the oranges I. and II. No hydrazone hitherto obtained has been a red dye, even the dihydrazones, the osazones being at most oranges. The authors describe the phenylhydrazone of β -naphthoquinone; orthophenylazo- α -naphthol; the transformation of β -benzeneazo- α -naphthol (hydrazone of β -naphthoquinone) into benzenedisazo- α -naphthol; the acetyldisazo- α -naphthol; and the ethylic and methylic ethers of disazo- α -naphthol.

On Certain Orthoxyazo-Derivatives of α -Naphthol and Hydrazones of β -Naphthoquinone.—E. Noelting and E. Grandmougin.—The authors describe certain orthoxyazo-derivatives of α -naphthol, which they have prepared in order to compare them with the para-azo-derivatives of α -naphthol. They are red colours, true ponceaus, whilst their isomers of the para series are browns, more or less inclining to yellow.

A Transposition on the Formation of the Diazo-Derivatives of α -Naphthol.—E. Noelting and E. Grandmougin.—The authors wish to compare the products obtained by the action of diazobenzol chloride upon the hydrazines of β -naphthoquinone, derived from sulph-anilic hydrazine, and the hydrazine of metamidobenzoic acid with those formed by the action of diazotised sulph-anilic and metamidobenzoic acid upon phenylazo- α -naphthol. The products were not identical as it might have been expected.

Action of Fluorine upon Phosphorus Trifluoride.—Henri Moissan.—If acted on by fluorine, phosphorus trifluoride passes at once into the pentafluoride. The reaction is attended with flame, like that of chlorine on phosphorus trichloride.

The Place of Fluorine in the Classification of the Simple Bodies.—Henri Moissan.—The author places fluorine at the head of the halogen family. There is, however, a difference in the respective behaviour of fluorine and chlorine with other elements. When fluorine combines with non-metals it forms compounds more volatile than the corresponding chlorides. When it unites with metals it yields products whose melting-point is higher than that of the corresponding chlorides. Calcium fluoride seems to approximate to calcium oxide more than to the chloride. Silver fluoride is very soluble in water, whilst the chloride is insoluble. Aluminium chloride is decomposed by water, whilst aluminium fluoride is insoluble and very stable. The fluorine ethers have always a higher boiling-point than the corresponding chlorine compounds; they are very stable, and less easily saponified. The action of fluorine upon the organic hydrogen compounds is so violent that no intermediate compounds are produced. Fluorine decomposes water in the cold, yielding ozone of such a concentration that it appears with the fine blue colour indicated by Hautefeuille and Chappuis.

TO CORRESPONDENTS.

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ENSOR DRURY, Registrar.

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SESSION 1891-92.

Faculties of Arts and Science.

The NEXT SESSION commences on WEDNESDAY, SEPTEMBER 30, 1891.

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THE CHEMICAL NEWS.

VOL. LXIV., No. 1659

ADDRESS TO STUDENTS.

In attempting to give anything in the shape of advice to students we are too generally met with the reply, "*Non possumus!*" If we exhort them to qualify themselves for extending the boundaries of any of the sciences, and for solving some of the difficult problems which each presents to us—in a word for research, instead of cramming for examinations—we are told that this is, in reality, advice to immolate themselves for the honour of their country and for the benefit of mankind. If we bid them give their attention to chemistry and physics, rather than to "classics," we find that in too many cases they have no option.

Schools and colleges are still organised on what might be called the mediæval type. Principals, masters, tutors of all grades, are selected from the ranks of those whom Mr. Arnold calls "the poor humanists," and who naturally give prominence to those studies in which they have themselves been exclusively trained. A few days ago there fell into our hands the prospectus of a day-school for boys on the Limited Liability principle. Its vice-presidents and its council consist largely of D.D.'s, Rev. M.A.'s, &c.; but there is in the list not a single D.Sc., Ph.D., or M.D. Nor do we recognise in the list the name of any man who has made his mark in the scientific world. The curriculum certainly includes "elementary science." But it is placed down towards the bottom of the list along with such disciplines as singing and shorthand. We fear that the amount of time and attention which it will receive will be very subordinate, and utterly out of proportion to its importance.

Now if a youth is educated at such establishments what chance has he for devoting his attention mainly to Science?

There is another way in which scientific studies are heavily handicapped by dint of the examination system. When a certain number of marks is required to gain some distinction, or when a position is open to the candidate who obtains the highest number, the total number to be gained by the utmost proficiency in the physical and natural sciences is fixed most unfairly low. What shall we say of an examination in which the maximum possible in organic chemistry was 250, whilst Greek and Latin might earn 400 each? What wonder if experienced "coaches" tell the student that science does not "pay," and that young men renounce their prospects of a brilliant reputation in the hope, instead, of earning scholarships, fellowships, and other tangible rewards of "passing." In the face of such conditions what boots the advice given by ourselves, as well as by men of higher standing? Charm we never so wisely, we address ears deafened by the instinct of self-preservation. Hence we find ourselves placed in a vicious circle, from which the student—especially the individual student—has little power of escaping. We should recommend him, however, wherever possible, to give his countenance and his sympathy to the friends of Mr. Auberon

Herbert, and to throw all the cold water at his disposal upon the examination system, its advocates, and its organs.

It is incumbent on every student of Science to earn freedom for himself and for those who may succeed him. The Jesuits, it will be remembered, first imported examinationism from its native China and acclimatised it in Europe. But even they did not bind down the pupils to one Procrustean curriculum, but they gave free course to different tastes and different capacities.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must have passed the Matriculation Examination. No exemption from this rule is allowed on account of Degrees obtained or Examinations passed at any other University. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June.

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must, not less than five weeks before the commencement of the Examination, apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Registrar, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination for the first time must pay a Fee of Two pounds to the Registrar. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him, but he shall be allowed to enter for any subsequent Matriculation Examination upon payment, at every such entry, of an additional Fee of one pound, provided that he comply with the Regulations in the preceding paragraph.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin. Any one of the following Languages:—Greek, French, German, Sanskrit, or Arabic. The English Language, and English History, with the Geography relating thereto. Mathematics. Mechanics. One of the following branches of Experimental Science:—Chemistry, Heat and Light, Magnetism and Electricity, Botany.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements; including their compounds, their chief physical and chemical characters, their preparation, and their characteristic tests.

A Pass Certificate, signed by the Registrar, will be delivered to each candidate after the Report of the Examiners has been approved by the Senate.

If in the opinion of the Examiners any candidates in

the Honours Division of not more than twenty years of age at the commencement of the Examination possess sufficient merit, the first six among such candidates will receive an Exhibition of thirty pounds per annum for the next two years; the second among such candidates will receive an Exhibition of twenty pounds per annum for the next two years; and the third will receive an Exhibition of fifteen pounds per annum for the next two years; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitor declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will be held July 18, 1892.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.SC. EXAMINATION.

The B.Sc. Examination will be held October 17, 1892.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

The examination for Honours in Chemistry will take place on Monday and Tuesday in the week following the Examination for Honours in Mathematics; on Monday by printed papers (chiefly on Organic Chemistry), and on Tuesday by practical examination in Qualitative and Quantitative Analysis.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Ex-

amination, upon a knowledge of which he rests his qualification for the Doctorate; and with this statement he shall transmit an original printed Dissertation or Thesis (at least six copies) treating scientifically some special department of the subject so named, embodying the result of independent research, or showing evidence of his own work, whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. The Dissertation or Thesis shall have been written in view of candidature, or shall have been published within the two academical years immediately preceding. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published, and every contribution so specified and submitted shall be considered and taken as part of his qualification for the Degree. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, and with especial reference to his Dissertation or Thesis.

Candidates for the Degree of D.Sc. will be expected to be so fully conversant with the branch of Science they profess as to be able, if required, to satisfy any test of their acquirements in that branch that it may be thought expedient to apply.

The Fee for this Examination is £10.

In October, 1892, modifications of these Regulations will come into operation, particulars of which can be obtained of the Registrar.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.*

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the third Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination. Not less than five weeks before the commencement of the Examination he must apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the Examination, accompanied with the candidate's fee.

The Fee for this examination is Five Pounds.

EXAMINATION IN SUBJECTS RELATING TO PUBLIC HEALTH.

A Special Examination will be held in December in subjects relating to public health.

No candidate is admitted to this Examination unless he has passed the Second Examination for the Degree of Bachelor of Medicine in this University at least one year previously; nor unless he shall have given notice of his intention to the Registrar at least two calendar months before the commencement of the Examination.

The Fee for this Examination is £5.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry.—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years, passing at least two examinations in Arts, and one in either Mathematics, Natural Science, Law, Modern History, or Theology, when, if he obtain a first, second, or third class, he can take his B.A. Degree; if he do not gain such honour he has to pass a third examination in *Literis Humanioribus*.

The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

* Candidates who pass in all the subjects of the Preliminary Scientific (M.B.) Examination, and also pass at the same time in the Pure and Mixed Mathematics of the Intermediate Examination in Science, or who have previously passed the Intermediate Examination in Arts, are admissible to the B.Sc. Examination.

Scholarships of about the value of £75 are obtainable at Christ Church, Magdalen, and other colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the University Calendar; from the professors; and from the Sub-Librarian in the Radcliffe Library or the Museum.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry.—G. D. Liveing, M.A., F.R.S.
Jacksonian Professor of Natural and Experimental Philosophy.—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in the first or third term of residence, or, through the Oxford and Cambridge Schools Examination Board, or through the Senior Local Examinations, before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £10 a year, are chiefly given for mathematical and classical proficiency. Scholarships are given for Natural Science in Trinity, St. John's, St. Peter's, Clare, Christ's, Sidney, Pembroke, Caius, Downing, and Cavendish Colleges; the examinations being in December, at Easter, and in June and October.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry.—J. Emerson Reynolds, D.Sc., M.D., F.R.S., V.P.C.S.

Assistant Lecturer.—Emil A. Werner, F.C.S., F.I.C.

Demonstrator.—William Early, F.I.C.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 1st of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy.*—Elementary, first year; advanced, second year.
2. *Organic Chemistry.*—General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The *Summer Course of Practical Chemistry for Medical Students* begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor

of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

KING'S COLLEGE.

(DEPARTMENT OF ENGINEERING AND APPLIED SCIENCE).

Professor of Chemistry.—J. M. Thomson, F.C.S.

Demonstrator of Practical Chemistry.—G. S. Johnson, F.C.S.

Assistant Demonstrator.—Herbert Jackson, F.C.S.

On Tuesday and Friday at 10.20 a.m. Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a View of the Forces which concur to the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic elements and their principal Compounds are described.

The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated.

Examinations of the Class, both *viva voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, on Tuesday and Friday, at 10.20, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis.

Any Student of this Department may be admitted to this Class at any period of his study on payment of an extra fee.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra Fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own Experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s. od.; per ann., £8 8s. od.; Practical Chemistry per term, £4 4s. od.; per ann., £10 10s. od.; Experimental and Analytical Chemistry—One Month (daily attendance), £4 4s. od.; Three Months (daily attendance), £10 10s. od.; Six Months (daily attendance), £18 18s. od.; Nine Months (daily attendance), £26 5s. od. A student taking a month's ticket may attend daily during 1 month, or 3 days a week during 2 months, or 2 days a week during 3 months.

Rules as to Admission of Students.

I. The Academical Year consists of Three terms: Michaelmas Term, from beginning of October to the week before Christmas; Lent Term, from the middle of January to the week before Easter; Easter Term, from Easter to the beginning of July.

II. The days fixed for the Admission of New Students in the Academical Year 1891-92, are Tuesday, September 29, Wednesday, January 13, and Wednesday, April 27.

METALLURGY.

Professor.—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is made to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery. The instruction given to each student is regulated by his special requirements.

PHOTOGRAPHY.

Lecturer.—J. M. Thomson, F.R.S.E., F.C.S.

Arrangements are made for a complete Course of Instruction in Photography to the students of the third year. A glass house has been erected, and in connection with it a Laboratory for the preparation of Photographic Chemicals. Students entering to this department will be afforded every facility for practising the Art in all its branches.

In addition to the regular College Course in Photography occasional classes are formed, consisting each of about six gentlemen, who meet twice a week. The fee for private instruction is £5 5s. for ten lessons, or £10 10s. for three courses. There is in every case a charge of £1 each course for chemicals.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the months from October to March, inclusive, and during the months of April, May, and June.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professor.—William Ramsay, Ph.D., F.R.S.

Assistant Professors.—R. T. Plimpton, Ph.D., and J. N. Collie, Ph.D.

Assistants.—C. F. Baker, B.Sc., and P. B. Williams.

The Session is divided into three Terms, as follows, all the dates being inclusive:—

First Term, from Friday, October 2nd, until Friday, December 18th;

Second Term, from Tuesday, January 5th, 1892, till Friday, April 1st;

Third Term, for Lectures, from Tuesday, April 26th, till Friday, July 1st. Class Examinations occupy about ten days, beginning on Monday, June 20th.

Junior or Matriculation Course.

Tuesday, Thursday, and Saturday, at 10, commencing October 7, 1891, and April 14th, 1892. Fee:—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Chemistry.

First and Second Terms: Inorganic.—The Class meets four times a week: Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises, commencing October 6th.

Fee:—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Intermediate Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9. The hour will be altered by special arrangement with the class if necessary.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Tuesday and Thursday, at 9, in the First Term; Tuesday, Thursday, and Saturday, at 10, in the Second Term; and Tuesday and Thursday, at 9, and Saturday, at 11, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who in studying the subject have not a Medical Examination chiefly in view. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course during the Second and Third Terms, instead of the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d. An Advanced Course for those engaged in prosecuting research in Organic Chemistry will be held three times a week during the Second Term. Fee, £2 12s. 6d.

Practical Class.

First and Second Terms, Tuesday and Thursday, at 11, commencing October 7th.

Fee, including cost of materials, £5 5s.; for a Second Course, £3 3s.

The Course includes the Practical Chemistry required at the Preliminary Scientific and Intermediate Science Examinations.

Senior Practical Class.

Wednesdays from 2 to 4 and Saturdays from 10 to 12 during the Third Term.

Fee:—(Including cost of materials) £5 5s.; for a Second Course, £3 3s.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London:—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Lectures on Chemical Technology may acquire here the requisite preliminary knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

A Gold Medal and Certificates of Honour are competed for by first year's Students. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1891-92; also the Clothworker's Scholarship of £30.

Chemical Technology.

Lecturer, Watson Smith, F.I.C., F.C.S.

Courses of Lectures will be given on the following subjects:—Manufacture of Sulphuric Acid, Alkali, &c. Fuel and Gas Manufacture. Chemical Technology of Building Materials. Coal tar Products and Colours. Applications of Chemistry to Engineering. Construction of Chemical Plant.

Evening Lectures will be given by gentlemen qualified by practical and theoretical acquaintance with special subjects, and occasional visits to Works will be arranged.

Residence for Students.

Students can obtain residence at University Hall,

Gordon Square. Particulars can be obtained at the office of the College.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor.—T. E. Thorpe, Ph.D., B.Sc., F.R.S.

Assistant Professor.—W. P. Wynne, B.Sc., A.R.C.S.

Demonstrators.—H. Chapman Jones and A. E. Tutton.

Assistants.—G. S. Newth, J. W. Rodger, and W. Tate.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. But students who are not candidates for the Associateship are permitted to take up the course of instruction in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, Geology, and Agriculture, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins on the 30th of September and ends about the middle of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidate being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first two years and in those of the special division he selects for his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the final examination in it receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
Chemistry	3	13
Physics	5	12
Biology with Botany .. .	5	12
Geology with Mineralogy .. .	4	8
Mechanics	4	6
Metallurgy	4	13
Mining	4	
Agriculture	4	10
Astronomical Physics .. .	2	

Mathematics and Mechanical Drawing, £3 per term.
Geometrical Drawing £3 per session. Freehand Drawing, £1 per term.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half the foregoing charges.

Associates of the Royal College of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

Bona fide teachers qualified to earn payments for teaching Science according to the rule of the Science Directory may attend any course of lectures on the payment of £1.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 200 teachers are admitted to them, and they receive 3rd class railway fare to and from South Kensington and a bonus towards their incidental expenses of £3 each. (See Science Directory.)

Working Men's Lectures.—Notification of these will be given in the newspapers.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Fiftieth Session will commence on Thursday, October 1st, 1891. Entries not previously arranged with the Dean may be made between 10 a.m. and 5 p.m. on that day.

Officers of the School:—Prof. Atfield, Ph.D., F.R.S., F.I.C., Practical Chemistry; Prof. Dunstan, M.A., F.I.C., Chemistry; Prof. Green, M.A., B.Sc., F.L.S., Botany; Mr. Joseph Ince, F.L.S., Pharmacy and Practical Pharmacy; Mr. Henry George Greenish, F.I.C., F.L.S., Materia Medica.

Dean of the School, Prof. Atfield, F.R.S.

Entries may be made for single classes. A bench in the chemical laboratories can be engaged at any time for any number of hours daily or days weekly for any period. Students are recommended to join the Lecture classes on Chemistry and Physics in October, but other convenient periods are the beginning of January or the commencement of the Second Course in April. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance on the Courses of Pharmacy also are accepted by the conjoint Board.

For Prospectuses, &c., apply to either of the Officers, or to the Dean, Prof. Atfield, F.R.S., at the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

Professor.—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Göttingen), F.I.C.

Demonstrator.—A. W. Warrington, M.Sc. (Vic.), F.I.C.

The College is open to male and female students above the age of sixteen years. The Session commences on Monday, September 27, on which day all Students will be expected to meet the Professors in the Library of the College.

Lecture Courses.—(1) Matriculation Course; two lectures weekly during the Lent and three during the Easter Term. (2) Intermediate Science Pass Course; three lectures weekly during the Lent and Easter Terms. For those Students who have selected Physics or Botany instead of Chemistry at the Matriculation Examination, an Introductory Course of three lectures weekly will be delivered during the Michaelmas Term. (3) Intermediate Science Honours Course; two lectures weekly during the Lent and Easter Terms. (4 and 5) B.Sc. Pass and Honours Courses; each three lectures weekly throughout the Session.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged to suit the requirements of the individual Student.

Students intending to proceed to the M.B. or B.Sc. Degree of the University of Edinburgh may count one or two years' residence respectively spent at this College.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 10s. per term, and for twelve hours, 20s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 15, and exhibitions are awarded at the end of the Session on the results of the class examinations.

The Chemical Laboratories in connection with this College have been recently built, and are fitted with every convenience for the prosecution of chemical studies.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, George McGowan, Ph.D., F.R.S.E. Assistant Lecturer in Agricultural Chemistry, F. C. Archibald.

Physics.—Professor, Andrew Gray, M.A., F.R.S.E. Demonstrator, David M. Lewis, M.A.

The Session opens September 30th, 1890. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the London University Matriculation Examination. Fee for the Term £2 2s. A class for revision of Matriculation Work will be held during the Summer Term. Fee for the Term, £1 1s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Term £2 2s.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s.

Medical Course.—Inorganic and Organic Chemistry. Fee for the whole Course, £4 4s.

Agricultural Chemistry.—Fee, £1 1s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours

per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s.

A Committee has been appointed to frame a complete scheme of Agricultural Instruction for North Wales, and the College has received a grant of £500 from the Board of Agriculture. Three Dairy Schools in connection with the College have been established in Welshpool, Denbigh, and Bangor, and an Agricultural Department is now open, in which students may receive a complete training in Agricultural Science.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE.

Professor.—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrator.—G. S. Turpin, M.A., D.Sc., F.C.S.

The Session commences October 5th, and terminates on June 24th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 55 lectures, and will cover the subjects prescribed for the London University Matriculation examination. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of 90 lectures in continuation of the Junior Course, and, together with laboratory practice, will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee £3 3s.

The Senior Course includes some 90 lectures devoted to Organic Chemistry; Fee, £3 3s.

An Elementary Organic Course of 10 lectures, and a course of 30 lectures on Qualitative and Quantitative Analysis will also be given.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 4-30; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Professors Thompson and Parker are recognised by the Universities of Edinburgh, Glasgow, and Aberdeen as teachers in Chemistry and Natural History respectively, so that registered Medical Students can spend one year of their course at the University College, Cardiff. The College is also recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of London or the Medical Courses at the Universities of Edinburgh, Glasgow, and Aberdeen, may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Female Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry.—Sydney Young, D.Sc.

Lecturer.—Arthur Richardson, Ph.D.

The session 1891-92 will begin on October 8th. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical

and electrical laboratory. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articulated pupils at reduced terms. Medical education is provided by the Bristol Medical School, which is affiliated to the College. Several Scholarships are tenable at the College. Full information may be obtained of the Secretary.

DAY LECTURES.

Inorganic Chemistry.

The Course treats of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Lectures will be given daily at 9 and 11 o'clock.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Lectures will be given during the Second Term on Tuesdays and Thursdays at 10 o'clock; during the Third Term on Mondays, Wednesdays, and Fridays at 10 o'clock. Fee, £3 3s.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it is closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures, and to Scouring, Bleaching, and Dyeing. The Laboratory is under the immediate supervision of the Professor and the Lecturer. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session ..	15	13	10	7½	5
" Two Terms ..	11	9	7½	5½	4
" One Term ..	6	5	4	3	2
" Month ..	3	2½	2	1½	—

Students may arrange to divide their days of laboratory work into half-days.

Analytical Course.

A Course of Lectures on the Principles of Qualitative Analysis will be given during the First and Second Terms; it is intended to supplement the instruction in Practical Chemistry. All first year's Laboratory Students are expected to attend this Course. The Lectures will be given on Mondays at 10 a.m. Fee, £1 1s. for the two Terms.

Photographic Chemistry.

Special arrangements can be made with regard to instruction in this subject.

Chemical Scholarship.—Among others, a Chemical Scholarship of £25 is offered for competition.

EVENING LECTURES.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at

which all the subjects required for the admission of Associates to the Institute are taught, and as a centre for the Practical Examination.

MASON SCIENCE COLLEGE, BIRMINGHAM.

Professor.—W. A. Tilden, D.Sc. Lond., F.R.S.

Assistant Lecturers.—W. W. J. Nicol, M.A., D.Sc. Edin., and Thomas Turner, Assoc.R.S.M., F.C.S.

Demonstrator.—T. Rhymer Marshall, D.Sc. Edin.

The Session will be opened on Wednesday, September 30th, 1891.

Elementary Course.

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. A Second Course of Twenty Lectures, having reference only to the subjects included in the syllabus of the Matriculation Examination of the University of London, will be given in the Summer Term. Lecture days—Wednesdays and Fridays at 11.30, Thursdays at 3.30.

Persons entirely unacquainted with Chemistry are recommended to attend the first of these Courses before entering for the General Course, which commences in October. Candidates for the Matriculation Examination of the University of London are advised to attend both these Courses.

General Course.

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms).

Candidates for B.Sc. and Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays from October to December, and on Mondays, Tuesdays, and Wednesdays from January to March, at 9.30 a.m. Fee, £5 5s. for the course.

2. April to June (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Tuesday, Wednesday, and Thursday at 9.30 a.m. Fee, £1 11s. 6d.

Advanced Course.

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet once or twice a week. Fee for the session, £3 3s.

Laboratory Practice.

The College Laboratory is open daily from 9.30 to 5, except on Saturdays, when it is closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees :—

	All day.	Three hours per day.
One Term	7 guineas	4½ guineas.
Two Terms	13 "	8½ "
Three Terms	18 "	12 "

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Metallurgy.

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each course. A more advanced course upon selected subjects is also given by Mr. Turner, the Lecturer in Metallurgy.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c.

Evening Classes.

Several Courses of Evening Lectures are arranged during the Winter and Spring Terms of each session. The subjects are treated in a less technical manner and the fees are nominal.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor.

BRADFORD TECHNICAL COLLEGE.

CHEMISTRY AND DYEING DEPARTMENT.

Professor.—Christopher Rawson, F.I.C., F.C.S.

Demonstrator.—(Vacant).

Lecturer on Botany and Materia Medica.—William West, F.L.S.

The school year is divided into three terms. The Session commences on September 14th and terminates on July 9th. The course of instruction extends over two years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters, technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Inclusive fee, £4 4s. per term.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day and for pharmaceutical students.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor.—Prof. E. Kinch, F.C.S., F.I.C.

Assistants.—James Hendrick, B.Sc. Lond., A.I.C., and W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation and stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the

properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY. THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry.—Arthur Smithells, B.Sc. Lond., F.I.C.

Assistant Lecturer in Organic Chemistry.—Julius B. Cohen, Ph.D., F.I.C.

Assistant Lecturer in Agricultural Chemistry.—Herbert Ingle, F.I.C.

Demonstrator.—J. H. Davies, B.Sc.

The Session begins October 6, 1891.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m., from October to the end of the second term, and during part of the third term. Fee for the Course, £4 4s.

2. Inorganic Chemistry.—First year Honours Course, Non-metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Inorganic Chemistry.—Second year Honours Course, Metals. Tuesday, Thursday, and Saturday at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 11.30 p.m. Fee £3 13s. 6d.

5. Organic Chemistry Honours Course.—Monday and Wednesday at 9.30 a.m. Fee, £2 12s. 6d.

6. Theoretical Chemistry.—Advanced Course. Tuesdays and Thursdays at 9.30 a.m. Fee, £2 12s. 6d.

7. Chemistry as Applied to Coal Mining.—Tuesday during the First Term, at 4 p.m.

8. Agricultural Chemistry.—Monday, Tuesday, and Friday, at 3 p.m., during first and second terms.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £18 18s.; five, £16 16s.; four, £14 14s.; three, £12 12s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Chemistry for Medical Students.—On Tuesday and Thursday, from 10 to 12 a.m., from May to July.

Practical Course in Sanitary Chemistry at times to be arranged.

Evening Class.

A Course of twenty Lectures by Mr. Ingle, on the Elements of Inorganic Chemistry (the Non-Metals) will begin during the first and second Terms, on Wednesdays, at 7.30 p.m., beginning October 14. Fee, 10s. 6d.

Dyeing Department.

Professor.—J. J. Hummel, F.I.C.

Lecturer.—L. Liechti.

Assistant Lecturers.—W. M. Gardner and A. B. Knagga.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Lecturer.—H. R. Procter, F.I.C.

The full Course, which extends over a period of three years, is suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of im-

portant works, and is recommended to sons of tanners. The Course includes instruction in chemistry, engineering, microscopy, leather manufacture, and practical work in the Leather Industries Laboratory.

Agricultural Department.

Professor.—James Muir.

The full Course occupies two years, and includes instruction in chemistry, physics, botany, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Cavendish, Salt, Akroyd, Brown, Emsley, Craven, and Clothworkers' Scholarships, and the Leighton Trustees' Exhibition, and one of the new 1851 Exhibition Scholarships. The West Riding County Council Scholarships are tenable at the Yorkshire College.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor.—J. Campbell Brown, D.Sc.

Demonstrators and Assistant Lecturers.—C. A. Kohn, B.Sc., Ph.D., T. L. Bailey, Ph.D., and W. H. Ince, Ph.D.

Assistant.—H. H. Froyssell.

The Session commences October 1st.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Course A.—Non-metals. Fee, £3 10s.

Course B.—Metals. Fee, £3.

Course C.—Organic Chemistry. Three Terms. Fee, £3.

Course D.—Physical Chemistry. One Term. Fee, £1.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Course F.—Technological Chemistry: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) Copper, Iron, and Steel. (3) Lead, Silver and Gold, Aluminium, and other Metals. (4) Distillation of Coal and Tar Industries. (5) Fuel. (6) Chemistry Applied to Sanitation. (7) Technical Gas Analysis. (8) Spectroscopy.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Special: For the Conjoint Board of Colleges of Physicians and Surgeons. (4). Senior: Practical Organic (Advanced Medical Class). (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Adulterations of Drugs and of Food, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class: Course arranged to suit the requirements of the London University B.Sc. Examinations, Pass and Honours, and for Inter-mediate M.B. Honours.

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical work.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study.

TABLE OF FEES.

Per Week.	One Month.	One Term, Three Months.	Two Terms, Six Months.	Three Terms, One Session.
One day ..	—	£4	—	£8
Two days ..	—	6	—	10
Three days ..	£4	8	—	12
Four days ..	4	9	12	15
Five days ..	—	10	14	18

Technological Curriculum.

Preliminary Year.—Chemistry, either the Elementary Course or Course A, according to the previous knowledge of the Student. Practical Classes 1 and 2. Mathematics, or Mechanics, or Physics. Engineering Drawing and Design (in this or one of the following years). French or German.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Practical Organic Class during the Summer Term; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German; Intermediate B.Sc. Examination may be passed. Engineering, First Year Course, Autumn and Lent Terms.

Second Year.—Chemistry, Lecture Course on Organic Chemistry, C, Lecture Course E or D, Technological Chemistry, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc. may be taken.

Third Year.—Courses D and F; part of Course C. Any other Courses omitted in a previous year. Laboratory, five days per week. Students may finally choose a special subject either of research or of applied Chemistry. The Examination for the Associateship of the Institute of Chemistry of Great Britain and Ireland may be taken. Three years study after passing the Preliminary Examination of Victoria University are required for the B.Sc. Degree in the Honours School of Chemistry.

Evening Classes.

Lectures will be given on the Products of the Destructive Distillation of Coal, Coal Gas, Coal Tar, and Ammonia; on Fuel; and on Practical Chemistry with Exercises.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, and a Sheridan Muspratt Exhibition of £25 per one year, will be awarded in December, 1891, on an Examination in subjects which are included in the first two years of the above curriculum. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

LIVERPOOL COLLEGE OF CHEMISTRY.

Principal.—George Tate, Ph.D., F.I.C., F.C.S.

The Laboratories are open daily from 10 to 5, excepting Saturdays, when they close at 1 p.m. The course of instruction is adapted to the requirements of students of Chemistry as a science, and in its applications to chemical and metallurgical industries. The fee for a three years' course of study is eighty guineas, or per session of three months eight guineas.

Prospectuses, containing full particulars of the day and evening classes, may be had on application at the College

DURHAM COLLEGE OF SCIENCE,
NEWCASTLE-ON-TYNE.

Professor of Chemistry.—P. Phillips Bedson, D.Sc., F.C.S.

Lecturer in Chemistry.—Saville Shaw, F.C.S.

Lecturer in Agricultural Chemistry.—W. C. Mackenzie, D.Sc. (Edin.).

The Session will commence on September 28th, 1891.

1. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science.

The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. A section of this Course will be devoted to an outline of Organic Chemistry. The class will meet on Mondays, Wednesdays, and Fridays, at 11.15 a.m., and will commence on Wednesday, October 7th.

Fee, £3 10s. for the Session.

2. *Advanced Course*.—Inorganic Chemistry, Tuesdays and Fridays, 3 to 4 p.m., during Michaelmas and Epiphany Terms.

3. *Organic Chemistry*.—A Course of about ninety Lectures will be given throughout the Session, the subject of which will be Organic Chemistry, or the Chemistry of the Carbon Compounds. This class will meet on Tuesdays and Thursdays, at 11 a.m., and will commence on Tuesday, October 8th.

Fee, £3 10s. for the Session.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for each course, £2 2s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m., commencing October 12th. Fee, £1 1s.

Metallurgy and Assaying.—A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry-Assaying, and in the preparation and analysis of Alloys, &c. Fee as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

A Lecture Course in Agricultural Chemistry will be given on Tuesdays and Thursdays at 10–11. Fee, Two Guineas.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees*.—Students working six days per week, £5 5s. per term; alternate days, £3 3s.; one day per week, £1 1s.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Physical Science. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.

2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Physical Science.—Every candidate for the Associateship in Physical Science will be required to satisfy the examiners in three, at least, of the five subjects,—Mathematics, Physics, Chemistry, Geology, and Biology,—in an examination, to be held at the beginning of his second year.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 29th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students.

OWENS COLLEGE, VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory.—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry.—C. Schorlemmer, LL.D., F.R.S.

Demonstrators and Assistant Lecturers.—Julius B. Cohen, Ph.D., and George H. Bailey, D.Sc., Ph.D.

Assistant Demonstrators.—A. Harden, M.Sc., Ph.D., and G. Fowler, M.Sc.

Lecturer in Dyeing and Printing.—Ernest Bentz.

The Session begins on October 6, 1892, and ends on June 24, 1893.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

General Chemistry.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 10.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honour Course.—Mondays, Wednesdays, and Fridays, 3.30 p.m., during the two Winter Terms. The Non-Metals.

Second Year Honour Course.—Mondays, Wednesdays, Fridays, 9.30, during the two Winter Terms. The Metals.

Third Year Honour Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (Honours).—Tuesdays, Thursdays, Saturdays, 9.30, during the Session.

History of Chemistry and Chemical Philosophy.—Thursdays, 10.30, during the Session.

An ordinary degree of B.Sc. in Chemistry, Victoria University, may be taken at the College in either two or three years, according as the student passes the Preliminary Examination on joining the College or whether he takes a year to prepare for that examination. The Degree of B.Sc. with Honours in Chemistry can be taken in three years, and the College Certificate in Technological Chemistry may be taken in the same time.

A number of important Exhibitions, &c., are available to students.

Technological Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—The Chemistry of Coal Tar.

Fourth Course.—Natural and Artificial Dye-stuffs.

Fifth Course.—Calico-printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Honours Course on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physic laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

UNIVERSITY COLLEGE, NOTTINGHAM. DEPARTMENT OF CHEMISTRY.

Professor of Chemistry—Frank Clowes, D.Sc. Lond., F.I.C.

Demonstrators.—J. B. Coleman, A.R.C.Sc. Dublin, F.I.C., and R. L. Whiteley, F.I.C.

Lecturers.—J. B. Coleman, F.I.C.; R. L. Whiteley, F.I.C.; C. Haydon White, M.R.C.S.; J. W. Carr, M.A.; and F. R. Sargeant.

The Classes of the College are open to students of both sexes above sixteen years of age.

The dates of commencement and end of Terms in the Session 1891-92 will be as follows:—First Term, October 5th to December 19th; Second Term, January 18th to April 9th; Third Term, April 25th to July 2nd.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Non-Metals for the first two terms and for Elementary Organic Chemistry in the third term. In his second year he takes the course on Metals for the first two terms, and Advanced Organic Chemistry in the third term. In his third year he attends a course on Applied Chemistry during the first two terms. Fee for Day Lectures and Classes, 50s. for the session of three terms: Non-Metals or Metals 42s.; Organic Chemistry (one term) 21s.; Applied Chemistry, 30s.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 2s. 6d.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry.—The chemical laboratory is open every day except Saturday from 10 to 5, on Saturday from 10 to 12, and on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation and in Qualitative and Quantitative Analysis; and students are enabled to work out the applications of Chemistry to Pharmacy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees.—For one term, £6; for the session, £15;

for day students for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for one evening per week, and 20s. for two evenings per week, per term.

Courses of Technical Chemistry Lectures are also given on Dyeing and Bleaching, Brewing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

A *Pharmaceutical Curriculum* extending over three Winter Sessions, includes Pharmaceutical Chemistry (lectures and laboratory work), Pharmaceutical Botany (lectures and class work on specimens), Materia Medica (lectures and use of specimens), and Practical Dispensing, taught by demonstrations and practical work in the laboratory.

Government Lectures and Classes.—Evening Lectures and Laboratory instruction will be given by the Demonstrators of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in October. Fee for each Lecture Course, 2s. 6d.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

FIRTH COLLEGE, SHEFFIELD.

Professor of Chemistry.—W. Carleton Williams, B.Sc. F.C.S.

Demonstrator and Assistant Lecturer.—L. T. O'Shea, B.Sc., F.C.S.

Assistant Demonstrator not yet appointed.

The Session will commence on Friday, October 2.

First Year's Course.—Chemistry of the Non-Metallic Elements. Monday, Wednesday, Thursday, from 10 to 11 a.m. Fee, £3 3s.

Second Year's Course.—Chemistry of Metals. Tuesday, Wednesday, and Thursday, from 10 to 11 a.m. £3 3s.; or for the First and Second Courses, £5 5s.

Third Year's Course.—Organic Chemistry, on Wednesday, from 9 to 10, and Saturday, from 10 to 11. Fee, £2 2s.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; two, 50s.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s.

UNIVERSITY COLLEGE, DUNDEE. (UNIVERSITY OF ST. ANDREWS).

Professor.—Percy F. Frankland, Ph.D., B.Sc. F.R.S., &c.

Assistant Lecturers and Demonstrators.—F. J. Hambly, F.C.S., and J. R. Appleyard, F.C.S.

The ninth session of the College will be opened on October 13th, 1891.

The Lectures and Laboratory practice in this University are recognised by the Royal College of Physicians and Royal College of Surgeons, London, and by the Royal College of Surgeons, Edinburgh, and for degrees in Science and Medicine by the Universities of Edinburgh, Glasgow, and Aberdeen.

The courses are suitable for the Degrees of the London University and for the Civil Service appointments, and will also satisfy the requirements of students in Pharmacy, and of students who intend to become candidates for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

Lecture Courses.

The object of these courses will be (1) to give systematic instruction in the general principles of the science, and information regarding the elements and their more important compounds; (2) to show how this knowledge may be usefully applied in the Arts and Manufactures.

A course of instruction in Practical Chemistry in the Laboratory is recommended to all who wish to obtain a sound knowledge of the science, and the methods of applying it to useful purposes—the duration of such course depending upon the special wants of the student.—The Professor will be glad to give any information to intending students.

First year's lecture course: General Chemistry (Non-Metals, Metals, and Elements of Organic Chemistry) (100 lectures), Monday, Tuesday, Wednesday, Thursday, and Friday, from 10 to 11 a.m.; fee, £3 3s.

Second year's lecture course: 1. Advanced Inorganic Chemistry, including modern Chemical Theory (50 lectures). 2. Organic Chemistry (50 lectures). Fee for the whole course, £3 3s.

A Lecture Course on Analytical Chemistry will be given on Saturdays, from 9 to 10. Fee, £1 1s.

Courses of lectures will be given on Dyeing, Bleaching, and the Chemistry of the Textile Fibres, with practical instruction in the Laboratory and Dyehouse. In connection with this Department there is an extensive Technical Museum, containing a large collection of specimens illustrating many branches of Applied Chemistry, and particularly the local industries.

Practical Chemistry (Laboratory).

The aim of the Laboratory Courses is to make the student practically acquainted with the science, so that he may conduct chemical analysis and original research, and generally to fit him for applying the science to the Arts, Manufactures, Agriculture, and Public Health. The courses are also arranged for students preparing for their medical and pharmaceutical examinations. A three months' course of practical instruction in Sanitary Chemistry for the B.Sc. Edinburgh, in the department of Public Health, may be taken in the College Laboratory.

The Laboratory will be open for students daily from 9 a.m. to 4 p.m., except on Saturdays, when it will be closed at 3 p.m. Each student on entering will be allowed to arrange his working hours to suit his own convenience, but will be required to keep the hours when once fixed.

Sessional Fees for Day Students:—The fees for both sessions are—for six hours per week, £3 3s.; each additional hour per week, 10s. 6d. Day students may not enter for less than six hours a week. Students joining the Laboratory during the second term will be charged two-thirds, and during the third term one-third of the above fees. Students may also enter for short periods, working every day in the week at the following fees:—For one month, £2 12s. 6d.; for two months, £5 5s.; for three months, £7 7s.

Evening Classes.—Courses of Lectures and Practical Laboratory instruction are given in Chemistry, Dyeing, and Bleaching.

Forster Research Scholarship.

This scholarship, of the value of £30, is awarded annually to the best student on the condition that he devotes himself during the ensuing year to original research in the College Laboratory.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor.—Alex. Crum Brown, M.D., D.Sc., F.R.S., Pres. C.S.

Assistants.—J. Gibson, Ph.D.; L. Dobbin, Ph.D.; H. Marshall, D.Sc.; J. Walker, Ph.D., D.Sc.; J. S. Murray, D.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to end of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. A class for advanced students is held in summer; it meets thrice weekly; fee £2 2s.

In addition to the above, Lecture Courses are given by the Assistants on special subjects, such as Chemical Theory, Physical Chemistry, or some particular branch of Organic and Inorganic Chemistry. These lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 10 till 4. (Fees: Winter Session, £10 10s.; Summer Session, £6 6s.) Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science must pass a preliminary examination in English, Latin, Arithmetic, Mechanics, Mathematics, and in two of the following subjects:—Greek, French, German, Higher Mathematics, Natural Philosophy, Logic, Moral Philosophy.

The First B.Sc. Examination embraces Mathematics, Natural Philosophy, Chemistry, Zoology, and Botany. The Second B.Sc. Examination (Section B, the Physical Experimental Sciences) includes Experimental Physics, Inorganic Chemistry, Organic Chemistry, Relation between Chemical and Physical Properties, Complex Qualitative Analysis (practical), and Simple Quantitative Determinations (practical).

A candidate for the D.Sc. Degree must submit a thesis on original work done by him, a historical or critical research connected with the special subjects of his Examination. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Section III. (Chemistry) will be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Professor.—W. H. Perkin, Jun., Ph.D., F.R.S.

Assistant Professor.—Arthur W. Bishop, Ph.D.

Demonstrator.—Bertram Prentice.

The Session begins October 1st, 1891.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Lecture Course in Chemistry is mainly devoted to Inorganic Chemistry. In the Laboratory course each student is required to prepare and study the properties of the principal elementary and compound gases; to perform the more important experiments shown by the Professor in the Lecture Room; to make himself thoroughly acquainted with the preparation and purification of salts, and with the tests employed in identifying these. After a careful study of the reactions of the principal metals and acids, he passes on to a complete course of the systematic qualitative analysis of simple salts and mixtures, and may then, if attending a second year, take up an extensive course of qualitative analysis (gravimetric and volumetric), ultimately making a speciality of any branch of the subject which may be most necessary for his future work. Great attention has been paid to the thorough equipment of the Advanced Laboratories, and special facilities are given to students who may wish to engage in any class of Research (Inorganic or Organic) whether of a purely Chemical or of a Technical nature.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following any industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Copies of the Calendar for 1891-92 may be had from Mr. John Young, B.Sc., the Secretary, 38, Bath Street Glasgow, price by post, 1s. 4d.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.
Professor of Chemistry.—T. Purdie, B.Sc., Ph.D., Assoc. R.S.M.

The Session begins on October 27th. A Competitive Examination, open to intending Students of Arts or Science, for a number of Entrance Bursaries, ranging in value from £40 to £10 each per annum, will be held during the last week of October. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), the regulations regarding which will be found in the "University Calendar."

Lecture Course.

A Lecture is delivered by the Professor of Chemistry, at 11 o'clock, on five days in the week throughout the Winter Session. The Course commences with the study of a few typical substances, serving as an introduction to the discussion of the Laws of Chemical Combination and the Atomic Theory; the Non-metallic and Metallic Elements, with their chief compounds, are then considered; and the latter part of the Course is devoted to Elementary Organic Chemistry. Three Lectures weekly are of an elementary character, and are intended to be useful to Students of Arts who desire to study Chemistry as a branch of general education, or with the view of teaching it in schools; the remaining two Lectures weekly constitute a Supplementary Course, framed so as to meet the additional requirements of

Candidates for the Degree of Bachelor of Science and of Medical Students.

Certificates are awarded on the results of separate examinations on the subjects of the general and supplementary Lectures, and the "Forrester Prize" of about £13 is awarded to the best Student of the year.

Fee for the Session, £3 3s.

Laboratory Course.

A class in Practical Chemistry meets for two hours weekly, to which Students attending the Lectures are admitted without additional fee. The Course consists of a series of qualitative and quantitative experiments, designed to give the Student a practical acquaintance with the principles of Chemistry regarded as a subject of general education.

The Laboratory is also open during the Session from 10 a.m. to 4 p.m., for instruction in Chemical Analysis. The fee is £10 10s. for the Session. Shorter Courses of Practical Chemistry are arranged to meet the requirements of Students who cannot give so much time to the subject, the fees for which vary according to the number of hours taken weekly.

Several free places in the Laboratory will be given to Students desirous of engaging in original work. Applicants must satisfy the Professor that their studies are sufficiently advanced to admit of them prosecuting experimental research.

The Laboratory is open for purposes of research during the summer months.

QUEEN'S COLLEGE, BELFAST.

Professor.—E. A. Letts, Ph.D., F.R.S.E., F.C.S.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week until the beginning of April, and on two days of each week after May 1st. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry.

II.—*Advanced and Organic Chemistry.*—Lectures on these subjects are given from the beginning of the Session, on Tuesdays and Thursdays, at 10 a.m., until the beginning of April, and at 3 p.m. after May 1st.

III.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses.

IV.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the beginning of April, and from May 1st until the middle of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

QUEEN'S COLLEGE, CORK.

Professor.—(The Chair is now vacant).

The Course of Theoretical Chemistry is divided into Inorganic and Organic Chemistry.

In the first part are discussed the Laws of Combination and Affinity, Molecular Chemistry, and the History of the Non-Metallic and Metallic substances.

In the Organic portion of the Course will be considered the subjects of Organic Analysis, Organic Series, Compound Radicals and Types, Metamorphosis of Organic Bodies, History of Special Animal and Vegetable Bodies.

In treating of the Laws of Chemistry, and the History of Inorganic and Organic Bodies those points will be chiefly dwelt upon which have a practical bearing in the Arts, Medicine, Engineering, and Agriculture. Thence, during the Course, attention will be directed to the application of Chemistry to Medicine and Physiology, to Metallurgic Operations, Chemical Manufactures, Building Materials, Soils, and Manures.

Fee.—For each Sessional Course, £2. Each subsequent Course, £1.

The Chemical Laboratory is open daily except on Saturdays, from 10 to 4 o'clock, under the Superintendence

of the Professor, to Students desirous of prosecuting an extended course of qualitative and quantitative analysis, and for the purpose of original investigation in connection with the Arts, or in the higher departments of Scientific Chemistry.

The Course of Practical Chemistry consists of about thirty-nine Lectures, and will commence at the beginning of the Second Term. Fee for each Sessional Course £3.

ROYAL COLLEGE OF SCIENCE FOR IRELAND, STEPHEN'S GREEN, DUBLIN.

(SCIENCE AND ART DEPARTMENT).

Professor of Chemistry.—W. N. Hartley, F.R.S.

Assistant Chemist.—T. A. Shegog, F.I.C., F.C.S., Associate of the Royal College of Science.

The Session commences on Monday, October 5th, 1891, and ends on June 22nd, 1892.

The Royal College of Science for Ireland supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Mining, Engineering, and Manufactures. The Diploma in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry, (2) Chemical Manufactures, (3) Metallurgy, (4) Analytical and Experimental Chemistry, (5) Instructions in Chemical Research.

Fees payable by Associate Students in the Faculty of Manufactures:—For the entire Course—first year, £13; second year, £23; third year, £14.

Fees payable by Non-Associates:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£2 for a special course of one month; £5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months; £12 for the entire session.

The following are supplementary courses of instruction for beginners:—

Laboratory Instruction in the Theory of Chemistry. A two-months' Course. By arrangement with the Professor the hours of attendance are fixed so as to suit, as far as possible, the convenience of the students, the laboratory accommodation being limited.

A Course of Lectures on Elementary Chemistry by the Assistant Chemist, February, March, April, and May, Wednesday, 3 to 4 o'clock. Fee for the Course, 10s.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College. There are also nine Royal Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years; three become vacant each year, and are competed for at the May Examinations of the Department of Science and Art.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—*Central Institution, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be pro-

vided in those kinds of knowledge which bear upon the different branches of industry, whether Manufactures or Arts. The main purpose of the instruction given in this Institution is to point out the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged.

Technical College, Finsbury.—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. The College embraces the following departments:—1. Mechanical Engineering and Applied Mathematics; 2. Electrical Engineering and Applied Physics; 3. Industrial and Technical Chemistry; 4. Applied Art; 5. the Building Trades. The College is under the general direction of the Principal. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College at 10 o'clock on Tuesday, September 29th, 1891, and the work of the Session will commence on October 7th.

BIRKBECK LITERARY AND SCIENTIFIC INSTITUTION, BREAM'S BUILDINGS, CHANCERY LANE.—*Chemistry:* Courses will be conducted, commencing October 1st, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University. *Inorganic Chemistry:* Mr. G. Chaloner, F.C.S. Lectures—Elementary, Tuesdays, 8.30 p.m.; Advanced, Thursdays, 7 p.m.; Practical, Tuesdays, 6–8 p.m.; Thursdays, 8–10 p.m.; Saturdays, 7–9 p.m. *Organic Chemistry:* Mr. F. Gossling, B.Sc. Lectures—Elementary, Wednesdays, 6.30 p.m.; Practical, Wednesdays, 7.30 p.m., Fridays, 6 p.m.

ST. GEORGE'S HOSPITAL MEDICAL SCHOOL (Chemistry Department).—Lecturer, Samuel Rideal, D.Sc., F.I.C., F.C.S. Arrangements have been made for a six months' Course in Public Health Instruction for gentlemen intending to present themselves for examination by the two colleges for the Diploma of Public Health.

CHARTERHOUSE SCIENCE AND ART SCHOOLS.—The Winter Session commences on Tuesday, September 22nd, 1891, under the presidency of the Rev. H. Swann, M.A. Classes are established in this institution by which instruction of a practical character is given in most of the Sciences at a very nominal fee; whilst in Art, at an equally low rate, Students, under the direction of five competent instructors, can be advanced in their studies. Those who have leisure can, at a very moderate charge, attend the Day Classes in Art. Day Classes will also be held to prepare Candidates for Matriculation (Lond.), the Clerical, Medical (including Dental), Legal, and other Examinations. Students who aim at becoming proficient in Chemistry (Organic and Inorganic) have the opportunity of working

in a well-fitted Laboratory, capable of accommodating sixty Students. Aspirants for University Honours can at a small expense be assisted in their studies.

THE CITY SCHOOL OF CHEMISTRY AND PHARMACY, 27, Chancery Lane, London, W.C.—Principal, Mr. Maurice Williams. Assisted by Mr. T. A. Ellwood, A.I.C., F.C.S., Mr. Martin J. Cole, and Mr. E. Hayward. Theoretical and Practical Chemistry, Chemical Physics, Theoretical and Practical Pharmacy, Materia Medica, Botany, Prescription Reading, Microscopy, &c.

MIDDLESEX COLLEGE OF CHEMISTRY AND PHARMACY, 40, Charlotte Street, Portman Place.—Principal, F. H. Painter. Day and Evening Classes and Laboratory Instruction in Chemistry, Pharmacy, Materia Medica, &c.

NEW CENTRAL SCHOOL OF CHEMISTRY AND PHARMACY, 173, Marylebone Rd., London.—Mr. J. Woodland, F.C.S., Lectures are given on Chemistry, Botany, Materia Medica, Pharmacy, Latin, and Physics. Laboratory instruction.

SOUTH LONDON SCHOOL OF PHARMACY, 325, Kennington Road, S.E.—Lectures on Chemistry and Physics, by Dr. John Muter, F.R.S.E., F.I.C., Daily, at 9 a.m. (Organic) and 10 a.m. (Inorganic). Lectures on Botany daily at 12 noon, and at 2 p.m. on Materia Medica and Pharmacy, by Mr. Dodd, F.C.S. The Laboratories for Qualitative and Quantitative Analysis open daily from 9 till 5, under the direction of Mr. de Koningh, F.I.C., F.C.S. The Students' Laboratory of this Institution is specially designed to accommodate 40 Students. The Technical Laboratory is open daily from 9 till 4, and is fully fitted with all apparatus for teaching the manufacture of drugs and chemicals. Periodical Examinations of the Students are held by Visiting Examiners appointed by the Council of Education, and Medals and Certificates are awarded on the results thereof. Fees for the first three months £10 10s. (junior) and £12 12s. (senior); afterwards £2 2s. and £3 3s. per month respectively, inclusive of all departments.

THE GOLDSMITHS' INSTITUTE, New Cross, S.E.—Head of the Chemical Department, Mr. A. G. Bloxam, F.I.C. Lectures and Practical Classes, also special classes in Chemistry as applied to various arts and industries, are held in the evenings from 7.30–10.0, and are open to both sexes. Session begins October 1st. Fees per Session (October to May): Theoretical Chemistry, 5s.; Practical Chemistry, 10s. 6d.

PEOPLE'S PALACE, Mile End Road, E. (Draper's Company's Institute).—Chemistry, Mr. D. S. Macnair, Ph.D., F.C.S. The classes are open to both sexes without limit of age.

ADDEY'S SCHOOL, Church Street, Deptford.—Head Master, William Ping, F.C.S.—Day and Evening Classes.

POLYTECHNIC INSTITUTE, 309, Regent Street, London, W.—Mr. R. A. Ward and Assistants.—Evening Classes in Theoretical and Practical Chemistry, &c.. The Classes are open to both sexes. The next term commences on Monday, September 28th, 1890.

WESTMINSTER COLLEGE OF CHEMISTRY AND PHARMACY, Trinity Square, Borough, S.E.—Messrs. Wills and Wootton. Day and Evening Classes.

BRISTOL MEDICAL SCHOOL.—Mr. T. Coomber, F.C.S.

THE CLIFTON LABORATORY, Berkeley Square, Bristol.—Conducted by Ernest H. Cook, D.Sc.Lond., F.I.C., F.C.S. Students are received either as Private Pupils or Members of a Class. Instruction is given to those requiring to use science or scientific methods in Commercial and Industrial pursuits, or in preparing for Examinations.

LEEDS SCHOOL OF MEDICINE.—Prof. Smithells.

LEEDS SCHOOL OF SCIENCE AND TECHNOLOGY, Rossington Street.—Head Master and Lecturer on Chemistry: Mr. S. J. Harris, M.Sc., F.C.S.; Lecturer on Metallurgy:

Mr. A. Burrell, F.I.C., F.C.S.; Lecturers on Chemical Technology: S. J. Harris, A. Burrell, and G. W. A. Teanby. Demonstrator in Chemistry: E. Rawlins, F.C.S. The courses of instruction are adapted to the syllabus of the Science and Art Department, but facilities are offered to those who desire to work for the London University exams., or to pursue some special branch of practical chemistry or metallurgy. The Chemical Laboratory is open for three nights per week, and the Metallurgical Laboratory for two nights. There is a special course of lectures for candidates for "Honours."

INSTITUTE OF CHEMICAL TECHNOLOGY, Hackins Hey, Liverpool.—Principal, Mr. A. Norman Tate, F.I.C. The course of instruction is intended more especially for students who wish to gain a knowledge of chemistry and the allied sciences in their relation to industrial and commercial pursuits, and embraces a thorough preliminary course of theoretical chemistry and practical laboratory work, followed by instruction in chemical technology fitted to the requirements of each pupil. In addition to these chemical studies, students who desire it can enter upon a special course calculated to afford them knowledge useful in the erection and arrangement of manufactories and plant, and construction of apparatus.

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THE CHEMICAL NEWS.

VOL. LXIV., No. 1660.

ON THE CAUSE OF IMPERFECTIONS IN THE SURFACE OF ROLLED COPPER ALLOYS.*

By THOMAS TURNER, A.R.S.M., Mason College.

THE greater part of this paper has already been published (CHEMICAL NEWS, vol. lxiii., p. 227). It has recently been suggested that the red stains examined by the author were possibly caused by the presence of iron, irregularly distributed through the alloy. The iron was asserted to cause electrical action during pickling, and to lead to local deposition of copper. The iron was supposed to be introduced by the workman, who generally uses an iron rod for stirring the metal in the crucible during the melting of the alloy. The author has conducted a number of experiments to test this matter, by adding different proportions of iron to zinc-copper alloys during melting, and also by rolling out a steel wire embedded in a brass ingot so as to get iron introduced in a definite and recognisable form. It would appear that iron itself has no such electrical action as has been suggested, either when alloyed or when merely embedded in the other metals. Iron rust, however, does cause a red stain on the surface of the rolled alloy, though this stain is possibly due to an absorption of the pickling liquor by the porous oxide; and the author has previously shown that the presence of a little of the pickling solution produces this effect.

Iron does not cause any red stain in yellow copper alloys if the oxide is rubbed off, or otherwise removed, at each re-heating. The fact that good surfaces are regularly produced with Delta metal, and other alloys containing iron, is regarded as proof of the correctness of the author's conclusions.

Since the previous paper was published other instances have been observed in which much trouble has been experienced from the presence of red stains on the finished metal, and in these cases, also, water rich in chloride was used for washing the sheets after pickling.

ACTION OF NITROSYL CHLORIDE ON UNSATURATED CARBON COMPOUNDS.*

By J. J. SUDBOROUGH, B.Sc., A.I.C., F.C.S.,
Associate of Mason College, Birmingham.

THE first investigations as to the action of nitrosyl chloride on carbon compounds were apparently made by Tilden. In 1874 this chemist studied the action of NOCl on phenol. He found that when dissolved in glacial acetic acid, and treated with NOCl gas, whilst kept in a freezing mixture, the greater part of the phenol is converted into chloranil, whilst small quantities of ammonium chloride are formed at the same time (Journ. Chem. Soc., 1874, vol. xxvii., 851). A few years later the same chemist investigated the action of NOCl on the terpenes. By acting on chloroform solutions of the terpenes kept at -10° he obtained compounds of the formula—



These compounds vary slightly in melting-point and other properties, according to the terpene from which they are prepared. By treating these bodies with alcoholic potash the elements of hydrochloric acid are withdrawn, and the substances known as isonitrosoterpenes are

formed (Journ. Chem. Soc., 1877, vol. xxxi., 554). Two years later Tönnies investigated the action of nitrosyl chloride on amylene and anethol (Berichte, 1879, vol. xii., 169). Both these bodies form addition compounds, viz., $C_5H_{10}NOCl$, and



By reduction the corresponding bases are formed, viz., $C_5H_{11}NH_2$, and



The following paper is a preliminary note on some experiments undertaken by myself during the past few months with the object of generally studying the behaviour of nitrosyl chloride towards unsaturated carbon compounds. Among the compounds which have been treated with the nitrosyl chloride are ethylene, propylene, amylene, cinnamene, crotonic, oleic, erucic and cinnamic acids. The nitrosyl chloride used throughout these experiments was prepared from dried common salt and nitrosyl sulphate. (Sudborough and Millar, Journ. Chem. Soc., 1891, vol. lix., 73).

Action on Ethylene.—Ethylene, which had been thoroughly washed and dried, was passed, together with the nitrosyl chloride, through a long spiral tube, and then through two U tubes cooled to about -15°. By this means a quantity of a red liquid was formed, the greater part of which was condensed nitrosyl chloride. After standing for some time the nitrosyl chloride passed off, and a yellowish oil boiling at 80° was left behind. Another portion was distilled straight away; it began to pass over at 15°, and the temperature gradually rose to 80°, when a small quantity of the same oil was left behind. As this oil was not decomposed by water, the original red liquid was treated with a very dilute alkaline solution, the nitrosyl chloride was thus decomposed, and the oil fell to the bottom. This oil was washed, dried, and distilled. As thus obtained it was a colourless, fragrant liquid, boiling between 81° and 84°. It was found to contain chlorine, but not nitrogen, and on analysis gave numbers which clearly showed it to be ethylene dichloride $C_2H_4Cl_2$. It also agreed with Dutch liquid in all its properties. The yield was small; after the two gases had been passing for four or five hours only about 10 c.c. of the oil were obtained. It thus appears that ethylene does not unite with nitrosyl chloride to form a stable compound, but is directly chlorinated, forming Dutch liquid $C_2H_4Cl_2$.

Action on Propylene.—Propylene obtained by the action of allyl iodide on ethyl alcohol and zinc, was treated in exactly the same way as ethylene. The red liquid thus obtained yielded only a very small quantity of oil. This oil possessed a very pungent odour, and was found to contain chlorine. Although the gases were kept passing for several hours sufficient oil was not obtained for analysis. When the propylene was allowed to bubble through liquid nitrosyl chloride, no compound of any kind was formed. In order to prove that the propylene used in these experiments was practically pure, a specimen of the dibromide, $C_3H_6Br_2$, was prepared and analysed. This compound was readily formed, and on analysis yielded good results. Hence it appears that nitrosyl chloride has practically no action on propylene.

Action on Amylene.—The following was found to be the best method of preparing the amylene nitrosochloride:—About 50 grms. of pure amylene are dissolved in an equal bulk of chloroform. The solution is kept at -10°, and the nitrosyl chloride gas is allowed to pass in. The liquid turns blue, and afterwards, when excess of nitrosyl chloride has been passed, a deep green. The chloroform is then evaporated off as quickly as possible, by pouring on to a plate, and blowing air through. A minutely crystalline substance, coloured blue, is thus obtained. It cannot readily be drained from a small quantity of oil formed at the same time, as it dissolves

* Abstract of a Paper read before the British Association, Cardiff Meeting, 1891, Section B.

again so readily on the slightest warmth. The best plan, therefore, is to dissolve the whole in the smallest possible quantity of alcohol, and allow to stand for several hours, when the nitroso-chloride crystallises out in large, colourless, prismatic needles. These are tolerably pure, but may be re-crystallised by spontaneous evaporation from alcohol as long needles, or from chloroform as large monoclinic tables. These crystals melt at 152° , and on further heating decompose. They are readily soluble in chloroform, ether, alcohol, lignon and water. On reduction they yield the compound $C_5H_{11}NH_2$, one of the amylamines.

Action on Cinnamene.—Pure cinnamene, obtained from cinnamic acid, was treated in exactly the same way as the amylene. The nitrosyl chloride was passed in until the liquid was a deep red and smelt strongly of the chloride. The solution was then poured into about twice its bulk of methylated spirit, and as the chloroform gradually evaporated off minute crystals separated out. These were obtained quite pure by dissolving again in chloroform and precipitating with alcohol. As thus obtained the substance is a snow-white minutely crystalline body. On analysis it yielded results which proved it to be cinnamene nitroso-chloride, $C_6H_5 \cdot C_3H_3NOCl$. It melts at 97° , dissolves very readily in chloroform and also in ether, is only very slightly soluble in cold alcohol, but dissolves in boiling alcohol and is insoluble in water. On heating above its melting-point it decomposes, leaving a black tar which smells strongly of bitter almonds. Up to the present no base has been obtained by treating with hydriodic acid, nor yet with sodium amalgam.

Action on Crotonic Acid.—A small quantity of crotonic acid was dissolved in chloroform and treated with the nitrosyl chloride, when kept below -10° . The solution became red at once, and soon smelt of nitrosyl chloride. On allowing the chloroform to evaporate away a colourless crystalline body was obtained. This melted at 68° , whereas pure crotonic acid melts at 72° . This substance was also found to contain neither chlorine nor nitrogen. Another portion of crotonic acid was dissolved in chloroform and placed in a sealed tube, when a quantity of nitrosyl chloride was condensed on it. The tube was then sealed, and heated to about 90° on the water-bath. On allowing the chloroform to evaporate away the greater part of the crotonic acid crystallised out unaltered (m.p. 70°), although a small quantity of an oily substance was found at the same time. It therefore appears that crotonic acid is unaffected by nitrosyl chloride at any temperature between -10° and 90° .

Action on Oleic Acid.—The chloroform solution, when treated with nitrosyl chloride at -10° , turned blue, and much heat was evolved. On evaporating off the chloroform a bluish solid was left: this was washed with cold alcohol and re-crystallised from chloroform. It separated out as white waxy plates, which melted at 86° . On analysing it gave results which agreed with the formula $C_{18}H_{34}O_2NOCl$. It dissolves readily in chloroform, is only slightly soluble in cold alcohol, and insoluble in water.

Action on Erucic Acid.—This acid was treated in exactly the same way as the oleic acid, and it yielded a similar compound. This body crystallised from chloroform in waxy plates which melted at 92° , and on further heating decomposed. Analysis showed it to have the formula $C_{22}H_{42}O_2NOCl$. It agrees with the corresponding nitroso-chloride obtained from oleic acid in most of its properties. Thus both oleic and erucic acids readily unite with nitrosyl chloride to form definite compounds.

Action on Cinnamic Acid.—A chloroform solution of cinnamic acid turned red at once when treated with nitrosyl chloride at -10° . The gas was passed in till the solution smelt strongly of nitrosyl chloride, and then the chloroform was evaporated off. The only product thrown down was the unaltered cinnamic acid. A chloroform solution of the acid was then heated with a quantity of liquid nitrosyl chloride in a sealed tube to 100° . On evaporating off the chloroform, colourless crystals separated

out; these were found to contain chlorine, and analysis showed them to have the formula $C_9H_8O_2Cl_2$. An alcoholic solution of cinnamic acid was treated with amyl nitrite and hydrochloric acid, but the cinnamic acid was thrown down unaltered by the addition of the HCl. Thus cinnamic acid appears to form no addition compound, but at high temperatures is merely chlorinated to the compound $C_9H_8O_2Cl_2$.

Conclusion.—From these few experiments no definite conclusions can be arrived at as to the reasons why nitrosyl chloride forms addition compounds with some unsaturated bodies, chlorinates others, and is apparently altogether without action on others. But by further and more detailed investigation it is possible that some law may be found which governs the action of the nitrosyl chloride, and this may probably be of some use in determining the constitution of the terpenes. Hence it is my intention to continue this work at some future date.

Mason College, Birmingham.

A NEW METHOD FOR THE DISPOSAL OF SEWAGE, WITH SOME REFERENCES TO SCHEMES NOW IN USE.*

By C. G. MOOR, B.A. Cantab.

I.

In concluding a paper on methods of sewage treatment read at Burlington House at the recent Hygiene and Demography Congress, Dr. Thresh asked this question: "Do any of the processes mentioned, or any combination of such processes, enable us to get rid of our sewage in such a way as to give rise to no nuisance, cause no danger to health, and this at a cost sufficiently reasonable, considering the importance of attaining such results?"

In the opinion of most experts at the present day, the only answer that can be given to this enquiry is an emphatic negative.

We can see this from a brief consideration of those methods that are now in use; they may be divided into three classes:—

1. Lime processes.
2. Processes in which lime is not used.
3. Irrigation.

1. The first of these classes may be briefly disposed of; the lime is used either alone or in combination with aluminous salts, or, as in Hanson's process, with the so-called sulphurous powder. In each of these cases a good effluent is the only thing aimed at, as the sludge is worthless.

It is also worthy of notice that where lime has been used to precipitate, it must also be added to press with. Under this head also comes the Amines process, in which herring brine is added to the lime with a view of sterilising the sewage.

2. *Processes in which Lime is not used.*—The best-known of these is the A B C, in which the sewage is precipitated by a mixture of clay, alum, and charcoal, with a little blood. A clear, inodorous, and tasteless effluent is produced, and the sludge is pressed without lime, dried, and ground; it is stated to contain 3 per cent of ammonia and 5 per cent of phosphates: both of these figures seem high if the manure sold has not been enriched by ammonia or phosphate. Much has been said for and against this process; at any rate it is better that the sludge, whatever it contains, should go on the land than have to be thrown away, as sometimes happens in the lime processes.

The International Sewage Purification Company precipitate with a mixture of magnetic oxide of iron and salts of iron, alumina, and magnesia. The effluent is

* Abstract of a Paper read before the British Association, Cardiff Meeting, 1891, Section B.

further purified by passing through a filter bed of gravel and polarite. The sludge, when pressed without lime and dried, readily crumbles into a fine powder, and should be of some value as manure.

Webster's Process, or Electrical Treatment.—The sewage travels along a trough in which are placed iron plates connected to the terminals of a dynamo. Water is decomposed, and some iron also passes into solution, precipitation takes place, and the effluent is said to be good.

3. *Irrigation.*—In cases where land is cheap and of suitable character this plan may be adopted with success. In most cases the first cost is great, and so is the cost of maintenance. It is a disputed point as to whether parasites may not be communicated to the animals feeding from the crops raised off unfiltered sewage, and it is certainly not advisable, as is sometimes done, to irrigate fields with untreated sewage, so that pools of putrefying matter are formed round which cattle are feeding.

In the case of London it would be practically impossible to get land enough to deal with the enormous volume of sewage, which is very greatly increased in wet weather; and though it may be said that this is in great part rain water, yet the dirt washed off the streets and the fungus torn from the sewers by the increased volume of water will render some method of treatment as necessary as if it were ordinary sewage.

II.

And now to come to the subject of this paper; the treatment I have to lay before you has been practically tested by me at experimental sewage works at Leyton. I have no very novel suggestions as to the precipitation of sewage, the originality of my method depending on the manner in which the sludge cake, produced by any precipitation process, may be converted into marketable products.

Let us consider the ordinary composition of sludge cake; it is roughly, in 100 parts,—

Water	25
Inorganic matter containing phosphates	20
Combustible matter containing nitrogen	55

The above figures refer to sludge cake that has been dried by exposure to the air for some days.

Now suppose we could afford to distil the cake in gas retorts, we should save the ammonia; but it could not pay unless one could produce a sludge very rich in ammonia, and then it would be saleable without further treatment. There is, however, a cheaper way of distillation than that I have just mentioned. A Mr. Rees Reece, in a patent a good many years old, described a method of obtaining tar, ammonia, acetic acid, and inflammable gas from peat: this process was in successful operation for some time. He employed a kind of lime kiln with a forced draught, connected to a series of condensers. The operation was conducted in such a manner that the material in the lower part of the furnace was kept in active combustion, its heat distilled the material directly above, and this in its turn gradually descended to serve as fuel for the succeeding charge. Thus nearly the same effect was produced as if the peat had been distilled in retorts, except that, instead of carbonised matter, ash was obtained. I have employed the same method for dealing with sludge cake, and have made experiments on a sufficiently large scale to show the possibility of practical working. A furnace was set up built of boiler plate, lined with brick, and fitted with a fan and condensers: this was kept burning for three weeks continuously, during which time it was fed with sludge cake alone, and this sometimes contained more than 30 per cent of water, as some came straight from the press. The sludge gives ample heat for its own distillation, and might also be used to raise steam in the same furnace if desired.

The ammonia comes over with the liquor just as in gas

works, together with a quantity of light buttery tar which floats on the liquor. The cakes are reduced to a fine ash, which, if the temperature is raised by increasing the blast, can be changed into clinker. A very slight blast is sufficient to distil with, merely enough to get the products of distillation through the condensers.

Now the first question that will suggest itself is, What portion of the theoretical yield of ammonia is actually obtained?

Eighty per cent was what I actually obtained with the apparatus I had there, and it is at least probable that more could be obtained with better apparatus.

If the blast is carefully regulated the uncondensed gases will burn, being of similar composition to what is termed "producer gas"; this might be employed in raising steam to drive the fan, pumps, &c., working up the ammonia liquor or distilling the tar. I had originally intended to mix the ammonia, fixed as sulphate with the ash, to form a manure for general purposes; this cannot be done if there is much free lime in the ash, as ammonia is disengaged too readily.

Here perhaps I ought to state the reasons which compelled me to give up working at Leyton (where I was treated with great kindness by the authorities). The first reason was the low value of the ash, which contained about about 60 per cent of calcium salts. This great excess is due to the addition of lime first to precipitate and afterwards to press with.

The lime also introduces another difficulty, and that is the production of clinker in the furnace. The temperature of the furnace must of course be kept up to that point at which inflammable gas is produced, and when this is done it is hard to avoid a certain amount of clinker being formed also.

In the case of some towns where clinker can be used this might be done, and the ammonia alone relied on as a source of income, since sludge cake, even as produced at present, will yield enough ammonia to do more than pay for its distillation in the manner described.

The uncondensed gases from distilling or baking sludge cake have an exceedingly unpleasant smell, and must be burnt to avoid creating a nuisance.

Some time ago experiments were made of burning cake made from London sewage in a kind of oven, built with partitions so that the heat from one assists the one next to it, fires being lighted successively. The cake burnt without difficulty, but the ash being of little value it was abandoned. I believe no attempt was made to collect the ammonia.

A few years ago some ovens were tried at Leyton for burning the sludge cake to obtain ash; they either did not attempt or were unable to obtain the ammonia.

There was little or no sale for the ash, and it was subsequently abandoned.

III.

As regards a method of precipitation to go with the method of utilising sludge cake which I have just detailed:—

It is obvious where a separate system is used for storm water the ash will be worth more, as it will not be so contaminated with silica and other mineral substances from the roads.

Of course what is wanted is a means of producing a sludge cake as rich as possible in ammonia and phosphate, at the same time without adding precipitants in any large quantity which would lower the percentage of phosphate in the ash. At the same time the pressing ought to be done without lime; this is possible, as it is done at Kingston.

I have not been able to make experiments on this subject, but it seems certain that the use of lime ought to be avoided at all costs, and I should be inclined to try carbonised sludge in powder mixed with salts of alumina and iron, after precipitation running the liquid through a bed of lumps of carbonised sludge; when this bed is too foul to use any longer it can be burnt in the furnace.

I was not successful in preparing carbonised sludge in the same furnace that I have spoken of, though I think it could be done in a larger one. The attempt was made to rake out a portion of the sludge after being carbonised, but before it was burnt to ash. At any rate, if this cannot be done the cost of carbonising sludge in closed retorts heated by the inflammable gases I mentioned would not be prohibitive.

It seems probable that by using a sufficient quantity of this carbonaceous material (which can so readily be renewed) a considerable degree of purity could be arrived at in the effluent.

Any seeds present in the sludge, which are sometimes very numerous, are of course destroyed in the furnace and any vegetable matter reduced to ash, so that potash contained in the solids suspended in the sewage is rendered available.

As to what proportion the resulting manure if the whole of my scheme were in operation would be by weight to the cake dealt with, it is not possible to speak with accuracy—it might probably be one-tenth.

At the present day it is fast becoming widely felt that it is the duty of towns to treat their sewage in some way, so that no injury may be caused to health, yet we surely ought not to rest content with processes which yield nothing but refuse. It is now many years since Liebig insisted on the need of maintaining a proper circulation of phosphates and ammonia if we wish our land to remain fertile, and this need instead of diminishing shows itself more clearly every day.

ON THE NATURE OF SOLUTION.

No. IV.

By J. ALFRED WANKLYN and WILLIAM JOHNSTONE.

CONTINUING our work we are now prepared with a tabular statement of sulphates, and a table of alkalis, and a table containing ammoniacal salts and organic acids.

The figures tell their own tale, and require very little comment at this stage of the enquiry.

Certain ammoniacal salts show a minus value for $i - i_1$ that means that expansion takes place.

Ammoniacal Salts.

	Sp. gr.	i_1 .	i .	$i - i_1$.
$(\text{NH}_4)_2\text{OSO}_3$	1.724	0.420	0.510	+0.090
NH_4NO_3	1.691	0.402	0.384	-0.018
NH_4Cl	1.449	0.310	0.280	-0.030

Organic Acids.

Oxalic acid $\text{C}_2\text{H}_2\text{O}_4 + 2\text{H}_2\text{O}$..	1.436	0.303	0.330	+0.027
Tartaric acid $\text{C}_4\text{H}_6\text{O}_6$	1.739	0.425	0.460	+0.035
Citric acid $\text{C}_6\text{H}_8\text{O}_7 + \text{H}_2\text{O}$..	1.515	0.340	0.372	+0.032
Succinic acid $\text{C}_4\text{H}_6\text{O}_4$	1.428	0.300	0.296	-0.004

Sulphate of Ammonia.

The specific gravity of the solid salt was found to be 1.724 at 20° C. A solution containing 25.00 grms. in 100 c.c. of the solution had specific gravity 1.127.

i	=	0.510
i_1	=	0.420
		0.090



Nitrate of Ammonia.

The specific gravity of the solid salt was found to be 1.691. A solution containing 21.980 grms. in 100 c.c. of solution had specific gravity 1.0844.

i	=	0.384
i_1	=	0.402
		-0.018

Chloride of Ammonium.

Specific gravity of the solid found, 1.449. A solution containing 10 grms. per 100 c.c. of the solution had specific gravity 1.028.

i	=	0.280
i_1	=	0.310
		-0.030

Laboratory, Fish Street Hill, E.C.
September 1, 1891.

IMPROVEMENTS IN CHEMICAL MANIPULATION.

By H. N. WARREN, Research Analyst.

Production of Platinum Crucibles.

PERHAPS no other utensil is more often required in the laboratory where mineralogical determinations have to be made than platinum vessels of varying sizes. All that is required is to select a circular piece of platinum foil of the required size, fold it twice, the same as for a filter-paper, and a platinum crucible is at once formed that can be used with even greater advantage than an original and costly crucible, and which, after the fusion and extraction of the same has been performed, may be, if desired, reopened and used as ordinary foil.

Gold and Silver Crucibles made.

Select a porcelain crucible of convenient size, and apply to the outside of the same a solution of pyroxylin in ether, dry it by blowing for a few minutes upon the surface;

Sulphates.

	Specific gravity.	i_1 .	i .	$i - i_1$.	
K_2OSO_3	2.63	0.620	0.784	0.164	$2\text{K}_2\text{OSO}_3 + 3\text{H}_2\text{O}.$
Na_2OSO_3	2.693	0.629	0.910	0.289	$2\text{Na}_2\text{OSO}_3 + 5\text{H}_2\text{O}.$
CaOSO_3	2.9	0.655	0.970	0.315	$2\text{CaOSO}_3 + 5\text{H}_2\text{O}.$
MgOSO_3	2.61	0.616	0.894	0.278	$\text{MgOSO}_3 + 2\text{H}_2\text{O}.$
FeOSO_3	2.62	0.618	0.975	0.357	$\text{FeOSO}_3 + 3\text{H}_2\text{O}.$
CuOSO_3	3.572	0.720	1.00	0.280	$2\text{CuOSO}_3 + 5\text{H}_2\text{O}.$
ZnOSO_3	3.40	0.706	0.952	0.246	$\text{ZnOSO}_3 + 2\text{H}_2\text{O}.$
NH_4OSO_3	1.724	0.420	0.510	0.090	$3(\text{NH}_4)_2\text{OSO}_3 + 2\text{H}_2\text{O}.$

Alkalis.

	Specific gravity.	i_1 .	i .	$i - i_1$.	
LiHO	1.495	0.331	1.116	0.785	$\text{LiHO} + \text{H}_2\text{O}.$
NaHO	1.923	0.480	1.068	0.588	$4\text{NaHO} + 5\text{H}_2\text{O}.$
KHO	2.00	0.500	0.841	0.341	$\text{KHO} + \text{H}_2\text{O}.$
CaH_2O_2	2.5	0.600	1.290	0.690	$\text{CaH}_2\text{O}_2 + 3\text{H}_2\text{O}.$
SrH_2O_2	4.0	0.750	1.230	0.480	$\text{SrH}_2\text{O}_2 + 3\text{H}_2\text{O}.$
BaH_2O_2	5.0	0.800	1.120	0.320	$\text{BaH}_2\text{O}_2 + 3\text{H}_2\text{O}.$

when dry, apply to the same either solution of argentic nitrate, as the case may be, or solution of auric chloride; suspend the same while still moist over a strong solution of sulphurous acid; a sufficiency of gas will at once escape to give it a metallic coating: when this is accomplished connect the same to a battery of required strength, employing the usual depositing solution of either metal as desired. A compact metallic crucible, of varying thickness in accordance with the time allowed, is thus obtained; the inner or porcelain crucible is now detached, by applying the flame from a Bunsen burner, the pyroxlin film being thus destroyed, forming a space between the two, by which both are thus freed from each other.

Flasks coated with Metallic Copper.

The usual method of coating flasks, or other like articles, with metallic copper is very tedious, the first operation being to render the surface rough by means of fluorides, and afterwards applying plumbago to the prepared surface in order to obtain a conducting material upon which to obtain a deposit. All this preliminary, however, may be viewed as unscientific and waste of time; all that is required is to generate, from a small hydrogen apparatus, a stream of antimony hydride, and allow the flame of the same to impinge upon the cold surface of the article in question. A deposit of metallic antimony is at once established, upon which a surface of metallic copper may be deposited by the usual method.

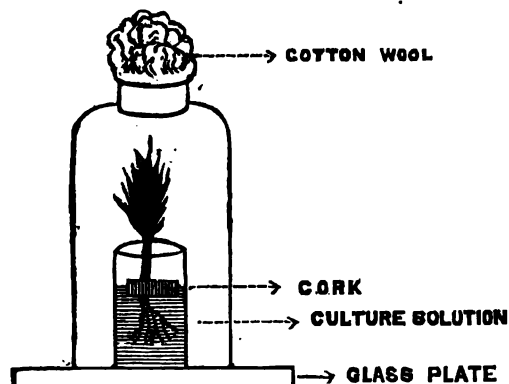
Everton Research Laboratory,
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ON THE DIRECT ABSORPTION OF AMMONIACAL SALTS BY CERTAIN PLANTS.

By A. B. GRIFFITHS, Ph.D., F.R.S.E., &c.

PROF. ACHILLE MÜNTZ (*Comptes Rendus*, vol. cix.; *Journ. Pharm.* [5], vol. xx.) has recently shown that the roots and rootlets of certain plants* are capable of absorbing salts of ammonia without first being converted into nitrates.

At the time of Muntz's researches I forwarded him a letter (dated Nov. 20, 1889), detailing some experiments which I had performed on the same subject, and which entirely confirmed his researches. However, it may be stated that my experiments were performed in a different manner to those of Muntz.†



Concerning these experiments (which are detailed below) he wrote to me as follows:—"Je suis heureux d'apprendre que vos expériences conduisent au même résultat que les miennes, quoique conduites d'une

* Beans, barley, hemp, and maize.

† Professor of Chemistry in the Institut National Agronomique, Paris.

manière différente. Votre méthode me semble tout à fait irréprochable et l'absorption directe des sels ammoniacaux, qui n'avait jamais été absolument démontrée, est aujourd'hui appuyée sur des preuves certaines."

These experiments were as follows:—

A large number of seedlings (beans) were immersed for thirty minutes in a solution of copper sulphate in order to destroy any nitrifying microbes present on the roots, stems, leaves, &c., of the young plants. After immersion the young plants were washed in sterilised distilled water, and the roots placed in sterilised culture solutions containing the following ingredients:—

Distilled water	1000 c.c.
Potassium chloride	1·00 gm.
Ferrous carbonate	0·03 "
Sodium chloride	0·50 "
Calcium sulphate	0·50 "
Magnesium sulphate	0·50 "
Tricalcium phosphate	0·50 "
Ammonium sulphate	0·50 "

The plants grew in sterilised glass apparatuses (see fig.†) which only admitted sterilised air,—that is, air which had previously filtered through plugs of cotton-wool (sterilised). The plants grew remarkably well for four weeks, although the nitrogen in the culture solutions was only in the form of ammonium sulphate, and nitrification was prevented.

The culture solutions were tested afterwards for nitric nitrogen by the Schloesing method (Griffiths' "Treatise on Manures," p. 362; Whittaker and Co.), but not the smallest trace of nitric nitrogen could be detected in the twenty-four separate culture solutions used in the experiments.

It may be stated that no nodules formed on the roots and rootlets of the bean plants during growth; hence there was no direct absorption of atmospheric nitrogen.

The culture solutions each contained 0·05 per cent of ammonium sulphate; but after the experiments this figure was reduced to 0·027 per cent.

It appears, from these experiments, that the nitrogen was absorbed as ammoniacal nitrogen by the roots of the plants, and not as nitric nitrogen; for microbes were excluded, consequently nitrification was rendered impossible.

In conclusion, there appear to be three sources from which bean plants derive their supplies of nitrogen:—

- (a). Nitrates in the soil (nitrification, &c.).
- (b). Atmospheric nitrogen (by the aid of microbes).
- (c). Ammoniacal salts.

If in nature the ammoniacal salts are, as a rule, first converted into nitrates, there can be no doubt that in certain cases they are also absorbed unchanged.

THE BACTERIOLOGICAL EXAMINATION OF WATER.

By Dr. G. FRANK.

THERE is no need of any further demonstration, that in order to decide on the suitability of a water for domestic and dietetic purposes its bacteriological examination is most prominently requisite. To fulfil this requirement in all cases has its peculiar difficulties.

For the purpose of chemical analysis a water may, without injury, be preserved for a considerable time, and hence it may be forwarded to an expert from a great distance, as the chemical properties of a sample of water change on keeping, only very slowly. With bacteria the case is very different.

* All the salts used were chemically pure.

† The bell-glass and glass plate were first washed in a strong solution of mercuric chloride, dried, and then heated to 130° C. in a hot-air steriliser.

If water is preserved in bottles there occurs a very rapid multiplication of the bacteria present, so that in some cases their number, even in a few hours, is many times greater than the number found immediately after drawing the sample (Meade Bolton, "Behaviour of Various Bacteria in Drinking-Water," *Zeitschrift für Hygiene*, vol. i., 76). As far as our present knowledge extends, this multiplication is not connected with the number and the kind of the bacteria originally present, with the chemical character of the water in question, or with external influences such as air and light, but it appears to us as purely arbitrary, i.e., the conditions and laws of this increase are as yet little known. We are, therefore, by no means able, from the number of bacteria found in water a certain length of time after sampling, to calculate back to the number originally present. Some observers have selected the variety and number of the different species found in a sample of water which has been retained as a character whence the quality of the water might be inferred. If even any determination of species—saving the exceptional cases in which pathogenic bacteria were present in the water—is of subordinate importance as compared with a determination of the number of germs, it is in every case, when water has stood for some time, and an increase of germs has consequently taken place, absolutely worthless. We now know that probably all bacteria, with perhaps the single exception of the bacillus of tubercle, can multiply in water; but we do not know the rapidity of this multiplication in the different kinds. Further, if a water containing many various species is preserved for a considerable time, we invariably observe that with the increase of the number of germs the multiplicity of species diminishes, so that ultimately there remains only a single kind, whilst all the others had disappeared. Hence there has been formed by natural selection a pure culture of the species which can best maintain itself, and multiply under the prevailing circumstances. Hence, in the case of a water which has stood for a certain time, we cannot assume that all the species which were originally present will still be found at the time of our delayed investigation; on the contrary, we must keep in mind the fact that a portion of them, i.e., those which increase more slowly, have already perished. Whether, therefore, in judging of a water we lay more weight upon the number of the germs or the multiplicity of the species, we must always be careful that no long time may elapse between the moment of cultivation and the installation of our culture-experiments.

In order to meet this demand, even in cases where a long time would pass between obtaining the sample and its arrival in the laboratory, the author has put together in a small box, all the apparatus which are absolutely necessary for the bacteriological examination of water. After having satisfied himself by prolonged experience of the simple management of this set of apparatus, he has undertaken with its means to have the culture-experiments executed by persons who have not had a bacteriological training.

The apparatus consists of (1) four flat culture-vessels closed with cotton-wool, of the form indicated and used by Fodér, Soyka, and Roszahegy; (2) a tin capsule with six short pipettes for 1 c.c.; (3) two bottles with well-fitting glass stoppers for taking the samples. All these utensils are sterilised and carefully packed in a small wooden box. This is then inserted in a larger wooden box, which in summer can be cooled with ice.

A.—Requisites.

The requisites are:—

1. The objects packed in the box.

(a) Four roundish bottles with flat sides, filled with nutrient gelatin (culture vessels); (b) a tin box with five pipettes; (c) two small bottles with glass stoppers.

The wadding plugs of the culture-vessels, the glass stoppers of the little bottles, and the lid of the tin box

must on no account be exposed to the air previous to actual use, or be drawn out of the necks of the bottles.

2. A washing dish with warm water at 35°. The temperature must be regulated by a thermometer.

The cultivation-vessels are plunged into this warm water so as to melt the gelatin. Particular care must be taken that the plugs of wadding are not moistened with the water.

3. A table or other horizontal support upon which the cultivation vessels are laid whilst the gelatin congeals.

4. Washing-water, soap, nail-brush, file for the nails, and clean towels.

5. In case of need crushed ice.

B.—Conspectus of the Process.

The entire operation resolves itself into:—

1. Liquefaction of the nutrient gelatin in the cultivation vessels by setting them in warm water.

2. Filling the small bottles with the water to be examined.

3. Taking a measured quantity of water out of the filled bottle by means of a sterilised pipette, mixing the water with the liquefied gelatin in the cultivation vessels, and stoppering the latter.

4. Letting the gelatin congeal.

5. Packing up the cultivation vessels.

C.—General Rules and Preparatory Manipulations.

1. In taking the sample of water for bacteriological examination, and in introducing the water into the cultivation-vessels, the most scrupulous cleanliness and the closest observation of the rules given are absolutely necessary.

2. For the experiment two persons are needed. One sees to the taking of the sample, and its introduction into the cultivation-vessels. The other undertakes to pump the water, or to purify the mouth of the pipe. He undertakes the liquefaction of the gelatin in the cultivation-vessels.

3. The water which has been stagnating in the pipes, or in the pump-well, must be removed before taking the samples of water. For this purpose, if the fittings are in perfect order, it is sufficient to let the water run out with the cock open to the full for ten minutes before taking the samples, or in the case to pump vigorously for the same length of time. But if visible impurities are detected at the overflow pipe they must be most carefully removed. In case of pumps the fittings must be in good condition.

4. The person who effects the sampling takes off his coat, turns up the sleeves of his shirt on both arms, and secures them so that they may not slip down accidentally. He then washes his hands and arms most carefully with soap and a brush up to over the elbow joint. Especial care must be taken in cleansing the finger nails, which are ultimately trimmed with the nail file. Finally the hands and arms are dried with a clean towel.

5. After both hands and arms are thus most thoroughly cleansed, one of the two small empty bottles is taken out of the box (which has been previously opened), in order to receive the sample.

N.B.—The second empty bottle serves as a reserve if the first has not been satisfactorily filled.

6. The bottle, still stoppered, is placed with one hand in the slowly-flowing stream of water. The stopper is then taken out with the other hand in the stream; the bottle is filled and lastly the stopper is re-inserted, still in the current of water.

D.—Charging the accompanying Cultivation-Vessels.

1. The glass stopper of the bottle which has been filled is taken off and laid upon the table with its flat top downwards. One of the two pipettes in the box is taken out and plunged with its pointed end into the bottle down to the bottom.

2. The water is let rise freely into the pipette from below until it stands above the upper mark.

3. When the pipette is thus properly filled, its upper end is firmly closed with the tip of the right fore-finger and the pipette is thus lifted out of the bottle. The glass stopper is then inserted in its place.

4. By cautiously lifting the forefinger, so much water is allowed to flow out of the pipette, that the level of the water in the pipette may exactly reach the upper mark.

5. The operator now draws out the plug of wadding with his left hand by a rotatory motion from the neck of one of the cultivation vessels (which the assistant has previously heated until the gelatin is liquefied), and retains it in his left hand.

6. The point of the pipette containing water is now inserted into the neck of the cultivation-vessel, and the water is allowed to flow out of the pipette (by easing the pressure of the right forefinger), until its level has fallen to the lower mark.

7. When this has been done the cultivation-vessel is again closed with its plug of cotton-wool.

8. The water is mixed with the gelatin by repeatedly inclining the cultivation-vessel gently, and this vessel is then placed upon the above-mentioned horizontal support (A, 3) until the gelatin has congealed.

9. The other cultivation-vessels are then supplied with water in exactly the same manner, using each time a fresh pipette. They are then, after the gelatin has thoroughly "set," packed up in the box in exactly the same manner as when they arrived.

10. If an irregularity has occurred in any of these operations the fact must be noted on the accompanying label, indicating the cultivation-vessel, the filling of which has been thus interfered with.

E.—Preservation, Packing, and Return of the Box.

The box when received is to be kept in a cool, but dry place. For its return a time of despatch must be selected such that it may be detained as briefly as possible on the way. The time of sampling and filling the cultivation vessels must be chosen so that it may be sent off as directly afterwards as possible.

In hot weather the box is placed in a chest with a double lining of sheet-metal. The space between the two sides is filled in the case with pounded ice, and on its return the water must be poured off and a fresh supply of ice introduced.—*Zeit. fur Anal. Chemie*, xxx., p. 305.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 124).

XXXIV.—Silicon.

1. SODIUM salts precipitate from fluoriferous solutions of silicon hexagonal prisms; tables and stars of 40–70 micro., hexagonal rosettes of 80–140 micro., all distinguished by distinct outlines, and a peculiar pale rose-red colouration. Highly dilute solutions deposit during evaporation at the margin of the drop crystals chiefly prismatic. Limit of the reaction 0.0005 m.grm. Si.

For many silicates it is sufficient to heat the specimen gently with hydrochloric acid and ammonium fluoride, after which we may at once proceed to precipitation with sodium chloride. If potassium is present it separates out, before the addition of the sodium chloride, as potassium silico-fluoride in very pale cubes of 10–20 micro. Further, titanium, zirconium, tin, and boron yield with sodium fluorides which are very similar to the fluosilicate. The volatility of silicon tetrafluoride renders it possible to avoid these difficulties by distillation with ammonium fluoride and sulphuric acid. Water or ammonium acetate

serves for receiving the distillate. If the presence of boron is suspected it is necessary to fractionate at about 140°.

2. From acid solutions of molybdic acid which have been heated with soluble silica, rubidium chloride precipitates a yellow crystalline deposit of rubidium silico-molybdate. (Compare Rubidium 1.) The reaction is extremely sensitive, but caution is required in its use. Its limit is at 0.000004 m.grm. Si.

The solution is fused with five volumes of soda, dissolved in nitric acid, adding ammonium molybdate and a little rubidium chloride. If phosphoric acid is present there is a speedy separation of yellow phosphomolybdate; otherwise it is heated to about 70° in order to form phosphomolybdate. It is better in order to escape deception by arsenic or by the separation of pulverulent molybdic acid to heat the liquid and only to add rubidium chloride if no precipitate has been formed. It must also be remembered that glass is perceptibly attacked by heating with strong acids, and that besides arsenic, antimony, vanadium, niobium, tantalum, and bismuth, react with molybdic acid similarly to phosphorus, whilst thorium, zirconium, titanium, and tin form compounds similar to silico-molybdic acid, and may thus be confounded with silicon.

According to a process previously indicated by the author, the silica of silicates which are decomposed by hydrochloric acid may be detected in thin sections, dyeing with a watery solution of magenta. This process is not suitable for flocculent silicic acid, as the preparations would have to be washed with a large quantity of water. Not all decomposable silicates behave in the same manner with dyes. Malachite green seems to act better than magenta.

XXXV.—Carbon.

1. From soluble carbonates the carbonic acid may be precipitated by salts of calcium, lead, or strontium. The finely pulverulent precipitate of calcium carbonate changes in a short time to small, well-formed rhombohedra. Lead carbonate crystallises more quickly in rods and lenticles of 15 micro.

Graphite and coal can be made fit for examination by combustion with 10 parts by bulk of saltpetre. As, notwithstanding all care, potassium nitrite is formed, salts of lead are here not applicable. Strontium nitrate reacts almost as quickly. Strontium carbonate forms globules of 6–12 micro. (Compare Strontium 4.) If pyrites are present salts of calcium must be used. Limit of the reaction 0.001 m.grm. C.

2. From insoluble carbonates the carbonic acid is expelled by strong acids in the form of a gas. The specimen is placed in a drop of water under a covering glass, a drop of hydrochloric acid is placed at its margin, and the water is absorbed at the opposite side with a slip of filter paper. Upon thin sections there are obtained both greater sensitiveness and localisation of the reaction. The latter may be increased as follows:—The specimen is covered with a solution of glycerin and gelatin in water, the layer is allowed to congeal and covered again after about 10 per cent of diluted hydrochloric acid has been added to the mixture.

XXXVI.—Boron.

1. In solutions of boric acid in hydrofluoric acid, or in hydrochloric acid and ammonium fluoride, potassium salts produce pale rhombs of 77°, or on slowly cooling, six or eight-sided tables and ridges, which are rather better defined. If the crystals are too pale they may be improved by re-crystallisation from hot water. Silicon, if it interferes, can be expelled by evaporation before the addition of potassium chloride, or by precipitation with barium chloride. Limit of reaction 0.0002 m.grm. B.

2. Ammonium fluosilicate, if sublimed with boriferous substances, yields fluoborate, which is treated as in 1. Limit at 0.0004 m.grm. B.

* *Zeit. Anal. Chemie*.

XXXVII.—Aluminium.

In solutions of aluminium sulphate which are not too dilute, salts of caesium produce the formation of well-developed colourless octahedra of caesium alum which measure 40–90 micro. Solutions containing more than 1 per cent aluminium sulphate yield dendritic structures, solutions with less than 0.2 per cent do not readily yield good octahedra.

If caesium chloride is used the solution of the sulphate must contain a little free sulphuric acid, but a large excess is injurious. Iron has no influence on the reaction. Limit at 0.00035 m.grm. Al.

2. Ammonium fluoride precipitates from neutral or slightly acid solutions of aluminium salts, pale, well-developed octahedra of 20–60 micro., soluble in nitric acid, but reproduced by ammonium acetate. The ammonium fluoride must be used in considerable excess, the solution of aluminium must contain no sodium and no iron. This reaction is equal in sensitiveness to the former, but it bears more dilution.

Aluminium hydroxide can be detected by means of dye wares. A watery solution of Congo-red is very serviceable. Care must be taken that the precipitate adheres firmly to the glass, so that the coloured preparation may be left in water for an hour.

XXXVIII.—Iron.

1. Potassium ferrocyanide gives a blue flocculent precipitate, the colour of which is distinctly perceptible under a magnifying power of 200 diameters. The limit of visibility is at the 5000th dilution of the iron salt, hence the limit of the reaction is 0.00007 m.grm. Fe. A large excess of strong acids must be avoided, as they can form Prussian blue from the reagent.

2. Ammonium fluoride precipitates ferric salts in the same manner as aluminium salts. The crystalline octahedra are colourless, with rather stronger margins than the crystals of the aluminium compound. The precipitation with ammonium fluoride is of more value for iron than for aluminium, as the iron in the crystals, after rinsing once with water, may be easily shown by means of ammonia. Conversion into Prussian blue does not give a good result. Limit of the reaction at 0.0002 m.grm. Fe.

3. Barium chloride and oxalic acid give in solutions of ferric chloride, instead of the short rods of barium oxalate, curved, curly, light brown hairs of 300 micro. in length. An excess of the reagents must be avoided. Limit of the reaction 0.0001 m.grm. Fe. Here also the behaviour of aluminium is similar, causing the formation of colourless tufts. The iron compound is coloured brown by ammonia and blue by potassium ferrocyanide.

XXXIX.—Chromium.

1. Silver nitrate, notwithstanding its rather lower sensitiveness, deserves the preference to lead salts, on account of the tendency of silver chromate to separate out from slightly acid solutions in large, characteristic crystals, which can be easily recognised along with precipitates of chloride, vanadate, &c. Concerning its properties see Silver 2. The limit of the reaction is at 0.000025 m.grm. Cr.

2. On lead chromate—compare Lead 4. It is difficult to obtain crystals, and the yellow colour of the finely granular precipitate, which appears only by reflected light, is readily overlooked. The limit of the reaction is at 0.00002 m.grm. Cr. Salts of chrome are preferably oxidised to chromates by fusion with saltpetre and soda, but in this manner the degree of sensitiveness mentioned above cannot be reached. The mean result was 0.0056 m.grm. Cr.

XL.—Vanadium.

1. Ammonium chloride added in excess to alkaline solutions of vanadic acid precipitates ammonium metavanadate in colourless lenticular crystals of 12–20 micro.

They polarise strongly with right extinction. Limit of the reaction 0.0003 m.grm. V.

2. Silver nitrate gives in solutions of vanadates acidulated with acetic acid a yellow precipitate, which, on heating with dilute acetic acid, are converted into orange rods of 10 micro. Limit of reaction 0.00007 m.grm. V.

XLI.—Niobium.

1. Soda-lye precipitates from alkaline solutions of niobic acid, and from solutions of the fluorine salts of fluorine, the salt $\text{NaNbO}_3 + 3\text{H}_2\text{O}$ in the form of colourless rods of 20–30 micro. They often coalesce in stellar groups, which may be mistaken for sodium tantalate. Hot water partially decomposes sodium niobate; it can be re-crystallised in free alkali. It is sparingly soluble in concentrated soda lye. The limit of the reaction is at 0.0006 m.grm. Nb.

2. The orange-red colour of niobic acid with tincture of galls and hydrochloric acid is of no value for the diagnosis of niobic and tantallic acid.

(To be continued).

DETERMINATION OF THE FINAL POINT IN THE TITRATION OF ZINC BY MEANS OF POTASSIUM FERROCYANIDE IN AN AMMONIACAL SOLUTION.*

By F. MOLDENHAUER.

THE author uses as indicator a 4 per cent solution of copper sulphate, with which he moistens a slip of very white and smooth filter-paper, 5 c.m. in breadth, in the following manner:—He draws a narrow longitudinal streak along the filter-paper by means of a hair-pencil saturated with the copper solution, and dries it quickly over a flame. Cross sections of this slip, of 2 to 4 m.m. in breadth, are cut off and enclosed in a stoppered bottle. For use, a drop of the precipitated solution of zinc is let fall upon the white end of such a slip. The liquid, in consequence of the capillarity of the paper, quickly travels to the blue part and soaks into it. If a small excess of ferrocyanide is present, there appears on the blue boundary line a red or reddish streak, the intensity of which increases with the quantity of the fluid that traverses the paper. If the excess is very slight, the reddish colour does not appear immediately. It appears, however, quickly and certainly if there is an excess of 0.1 to 0.2 c.c. of a decinormal solution of ferrocyanide in 100 c.c. of ammoniacal water. The appearance of the red streak is perceived the more easily the lighter is the laboratory, the whiter the paper and the background,—e.g., white porcelain. Recently prepared paper is more sensitive than such as has become old, but the latter becomes sensitive again in a moist atmosphere containing acetic acid. Good lamp-light, with a screen of opal glass, does not interfere with the detection of the reaction.

The titration may be performed either in heat or in cold. The author generally operates in heat.

The strength of the solution of ferrocyanide is so adjusted that 1 c.c. corresponds to 0.005 grm. zinc. The stoichiometrical relation requires 16.2615 grms. ferrocyanide to 1 litre. If the standard of the solution is checked with potassium-zinc sulphate it is always found a little too strong, whence the author uses the factor 1.01 in order to calculate the c.c. used, which exactly corresponds to 0.005 grm. zinc.

Potassium ferrocyanide at the dilution employed for titrating zinc is at first almost colourless. Very soon, however, it turns of a gold-yellow, and if kept for a long time it deposits a slight quantity of ferric oxide. This

change is avoided by adding 1 to 2 grms. of caustic potassa to 1 litre of the solution, and preserving it in bottles of a dark colour.

The titration of zinc is interfered with slightly by the presence of much ferric oxide, but considerably by manganese and magnesia.

In the latter case the author employs the following process:—He dissolves 2.5 grms. of ore in hydrochloric acid, and dilutes without filtration to 250 c.c. An efflux burette is rinsed twice or three times with about 5 c.c. of this solution, 60 c.c. are poured into the burette, and 50 c.c. are then run out into a small flask. To this quantity there are then added 10 c.c. ammonia and 5 c.c. of a solution of ammonium carbonate, containing, in 100 c.c., 5 grms. solid ammonium carbonate, 5 grms. sal-ammoniac, and 10 c.c. ammonia. It is heated until a dense precipitate subsides, and is set aside to cool. In the meantime the efflux burette is again filled with the original solution, 25 c.c. are poured into a beaker along with 10 c.c. ammonia, and the consumption of ferrocyanide is determined to 1 c.c.; 25 c.c. more of the original solution are added, and the mixture is titrated accurately. If the final point is exceeded, a few drops of the solution of the ore are again added, and the final reaction is once more produced, noting the quantities consumed of both solutions.

In the meantime the contents of the flask first mentioned will have cooled sufficiently. To the ammoniacal solution there are added 1 or at most 2 c.c. of a 10 per cent ammoniacal solution of sodium phosphate. The whole is shaken up for a short time and is then titrated,—that is after all manganese and magnesia present have been eliminated. If both are not present the result will agree with that first obtained, otherwise the latter result must be accepted as correct.

Before the experiment is regarded as decisive it is well, after a short time, to ascertain whether the final reaction is permanent; in some cases a few more tenths of a c.c. of the ferrocyanide solution must be added.

Manganese also can be titrated by means of ferrocyanide if no other bodies are present which are precipitated by the same reagent. To this end a measured quantity of a decinormal solution of potassium ferrocyanide is mixed with sal-ammoniac and ammonia, and the faintly acid or neutral solution, manganous solution, is dropped into the solution of ferrocyanide until the reaction on the slip of copper-paper just ceases to appear.

The highest quality made in Ireland is that of Larne, 22 candle. The poorest Irish gas is that of Magherafelt, 12 candle.

In Wales, Amlwch takes the lead with 23-candle gas, but elsewhere the highest standard reached is 19-candle.

A very useful feature, which might be obtained from the corporation and local boards, would be the maximum limit of sulphur permitted.

The Gas and Water Companies' Directory, 1891. Edited by CHARLES W. HASTINGS. London: Hazell, Watson, and Viney, Limited.

THIS publication, which has now reached its fifteenth year, has a distinct field from its companions, the Gas and Water Works Statistics. It gives, in parallel columns, the name of each town concerned, the date of formation of the gas or water undertaking, the special Acts (if any), total share capital, dividends, total loan capital; names of chairman, manager, and secretary; population, distance from London, and railway by which the town is reached. In the many cases in which the undertakings are the property, not of a company, but of the rate-payers, some of these items are necessarily absent. The dividends seem in many cases exorbitant for undertakings which are sure of a constant demand, and which cannot be troubled with bad debts, dead stock, or changes of fashion. The corporations which own gas or water works, or both, number 159, whilst 85 local boards are in the same position.

A new feature is a directory of electric-light installations, showing the capital invested, the system, capacity, price per unit, name of electrician in charge, and the area of supply.

The reader may be surprised to find that some of the most important and energetic cities, such as Birmingham, Leeds, and Manchester, have not adopted the new source of light.

An appendix gives the amount of local taxation paid by the gas and water installations.

Attempt at a Theory of the Sun and of the Variable Stars. (Essai d'une Théorie du Soleil et des Etoiles Variables.) By A. BRÉSTER, Jun., Sc.D. Delft: J. Waltman.

THE author ascribes all the phenomena of sun and the variable stars to a single cause—the intermittent chemical combination at the (comparatively) cool exterior of matter which had previously dissociated by heat. He regards the sun as displaying the stratified structure which gravitation gave it at the time of its formation. It is characterised by its imposing tranquillity. The protuberances which are regarded as the effects of terrible perturbing currents have in reality deceptive appearances, and are merely transitory lights.

The Foundations of Chemistry. (Grundlagen der Chemie.) By D. MENDELEEFF, Professor at the University of St. Petersburg. Part 6. St. Petersburg: Carl Ricker.

THIS part continues the study of the reputed elements, from mercury, including the bodies of the 3rd, 4th, and 5th groups as far as antimony. At the close of the 16th chapter the author suggests that his predicted element, eka-cadmium, may possibly be the "Norwegium" which Dahl discovered in the island of Krageiö. He considers, however, that further investigation is here necessary. Mention is here also made of Phipson's "Actinium" (1881), concerning which, however, nothing has been heard since 1882.

The origin of the vapours which issue from the earth charged with boric acid is pronounced for the present inexplicable, pending more general researches.

In the section on aluminium we find analyses of four Russian soils, in none of which do we find any alumina

NOTICES OF BOOKS.

Gas-Works Statistics, 1891. Edited by CHARLES W. HASTINGS. London: Hazell, Watson, and Viney.

IN the production and sale of gas no very important changes have been made. The gas varies very widely both in illuminating power and in price. In the former respect Milnthorpe takes the lead with a power of 23. Southport makes gas at 21.5, and Liverpool at 21.25. Thrale is near the bottom of the scale with 12-candle gas, for which it contrives to obtain 6s. 8d. per 1000. The prices of gas in different towns seem to have little relation either to the local cost of coal or to the scale of the operations. We notice two towns, Mottram and Mossley, both situate near to coal-mines and both having railway communication; yet Mottram vends 10-candle gas at 6s. 3d., whilst Mossley produces 10.4-candle gas for 3s. The information supplied by the gas producers is more complete than that furnished by the water undertakings.

In the illuminating power of gas Scotland still takes the lead. That of Banchory has 33-candle power; Colinsburgh, made from oil, 65; Eyemouth and Tain, each 32; whilst upwards of twenty towns supply a 30-candle gas. The lowest quality we find is that of Dollar, 22-candle; that of Glasgow is 33.

mentioned as present! The celebrated "black earth" from the province of Simbirsk is given as containing, in 10,000 parts of the air-dried sample,—

Na ₂ O		11
K ₂ O		58
MgO		92
CaO		134
P ₂ O ₅		7
N		44
S		13
Fe ₂ O ₃		341

The characteristic of this soil seems to be the large proportion of ferric oxide. The other three soils—described respectively as clayey, sandy, and peaty—are also not said to contain any alumina. We can only suspect here a clerical or typographical error.

The author adopts as convenient Graham's terms "hydrogel" for gelatinous hydrates, and "hydrosol" for soluble hydrates. He shows that compounds of alumina, &c., with bases, are evidently, like solutions and alloys, determined by similarity, and form a transition from mixtures to the type of the true salts.

We find it mentioned that alunite like that of La Tolla occurs in large masses in Transcaucasia.

The author is of opinion that the method of Ste. Claire Deville is still the most advantageous for the production of aluminium and its alloys.

Concerning the detection and separation of the rare earths we find no new information. The method of Crookes—the examination of the electro-phosphorescent spectra of the earths in high vacua—is substantially pronounced too sensitive, as being affected by the minutest admixture of the oxides. The recently discovered elements of didymium—*e.g.*, Welsbach's neodymium and praseodymium—are regarded as possibly mixtures.

The observations of Graham (1861–1864), on the transformations which the soluble and the gelatinous forms of silica respectively undergo, are pronounced as ranking among the most important steps towards an explanation of the formation of organic structures.

A passage occurring as a footnote at the end of the 16th chapter merits especial notice. The author writes:—"I consider it is suitable here to make mention of the absence of an element between cadmium and mercury. But as not one element is known in the 9th series of the periodic system, it is possible that only elements belong to this system which are *not capable of existence*." Not capable of existence on our globe, but perhaps possible in other heavenly bodies? This we submit is an extraordinary passage to have proceeded from the pen of a chemist who does not recognise the evolution of the elements as possible.

CORRESPONDENCE.

AN EXAMINATION MUDDLE.

To the Editor of the Chemical News.

SIR,—The Science and Art Department, in the recent examination in Honours Practical Chemistry, gave a brass wire in which students were told to estimate the quantity of copper, an outline of the process to be followed being given. It seems, however, that this work was beyond the scope of the Syllabus, and, in many cases, beyond the capabilities of the students. The wire contained about 65 per cent of copper, and the results varied from 20 to 90 per cent, and many students never made an estimation at all.

Owing to the remonstrance of teachers and students, who protested against anything not in the Syllabus being given, the examination seems to have been decided on

the results of the qualitative analysis alone, and we have the curious spectacle of students about 40 per cent out in a copper estimation passing in "Honours," and consequently certified as *qualified* to teach chemistry including quantitative analysis.

The examination in Honours must consequently have been easier than that of the Advanced Stage, which, in addition to a similar qualitative analysis, includes a written paper of questions.

Two of my own students (one in Honours and the other in the Advanced Stage) got exactly the same qualitative work, and both did it correctly. The Honours student, however, did not make his quantitative analysis, and the other seems to have been very weak in his answers to the paper of questions. The result of the examination is that the Honours student has obtained a second class, while, in the lower or Advanced Stage, the student who *did exactly the same work has failed*.

The facts are admitted by the Department, who, however, do not seem to see any absurdity in the same work passing one student in the higher and failing another in a lower stage.

Whatever value that might have been attached to the Honours certificate has surely been lowered by this action of the Department, and an injustice done to students who have obtained their certificates in former years.—I am, &c.,

TEACHER.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 9, August 31, 1891.

This issue does not contain any chemical matter.

Bulletin de la Société Chimique de Paris.

Series 3, Vol. vi., No. 2.

On the Use of Ammonium Sulphoselenite for Distinguishing the Alkaloids.—Prof. Ferreira da Silva.—This paper will be inserted in full.

A New Procedure for Extracting the Colouring-Matter of Natural Wines.—Louis Hugouenq.—The author uses the reagent of Roos, a solution of tartaric acid at 1/10, which is neutralised with a slight excess of ammonia and mixed with neutral lead acetate, until the lead precipitate ceases to dissolve. It is allowed to settle and filtered; the reagent is then poured into wine neutralised with ammonia as long as a precipitate is formed. This precipitate, collected and washed, is suspended in a small quantity of alcohol at 80°. Dilute sulphuric acid (about 15 per cent) is then added, avoiding excess. The liquid takes an intense red colour, and lead sulphate is precipitated and filtered off after standing for some hours. The alcoholic filtrate is mixed with 20 vols. of pure water. Almost all the colouring-matter is immediately precipitated. It is collected, washed, and dried at a low temperature. It is purified by re-dissolving it in alcohol and evaporating the solution *in vacuo* over sulphuric acid. The method may be successfully applied for extracting the colouring-matter of lyes.

On Diethylamidocaproic Acid.—E. Du villier.—The copper salt of this acid corresponds to the formula, C₂₀H₄₀N₂CuO₄. The free acid is obtained by treating the copper salt with sulphuretted hydrogen and allowing the solution to crystallise.

On Hydroxanthranol.—C. E. Lineberger.—Levi and Bach, on causing benzyl bromide to react upon the reduc-

tion products obtained by means of zinc powder in an alkaline solution, obtained benzyloxanthranol. If the chloride is used instead of the bromide we obtain a body containing two hydroxyles, and corresponding to a term of reduction of anthraquinone which has not been previously prepared.

The Oxidation of the Azo-Compounds.—Ch. Lauth.—The author's experiments furnish a means of distinguishing the azo-compounds by their transformation into diazos, which under the influence of suitable reagents yield colouring-matters. The distinctness and rapidity of this reaction may be used analytically, and yield also a rapid means of obtaining the quinones in a state of purity.

Apparatus for Luminous Projection applicable to Balances of Precision in order to obtain Rapid Weighings.—A. Collot, Jun.—This paper requires the accompanying illustration.

Series 3, Vol. vi., No. 3.

Constitution of Caprylic Aldehyd.—A. Béhal.—Caprylic aldehyd is certainly, as generally admitted, at present normal methylhexylcetone.

Action of Benzyl Chloride upon Ortho- and Para-Toluidines.—Ch. Rabant.—An account of the sulphonic derivative of benzylorthotoluidine, of benzylparatoluidine, and of benzylbenzylparatoluidine.

Action of Light upon Silver Chloride.—M. Guntz.—The substance of this paper has been already noticed.

Observations on a Memoir by Mr. Richards.—M. Guntz.—A controversy arising out of a paper contributed by Mr. Richards to the *Journal of the Franklin Institute*.

The Precipitation of Copper by Iron and the Action of Metallic Iron upon the Solutions of the Ferric Salts.—J. Ch. Essner.—Burnt copper pyrites, if alternately moistened and dried in the air, and afterwards exhausted with water yield a solution containing copper sulphate and ferric salts. If these solutions are treated with metallic iron at 70–80°, we obtain a deposit of metallic copper contaminated with a mud which is not easily removed. This mud was exclusively formed of ferric hydroxide. The copper, according to the quality of the iron employed, appears either as dust, as grains, or as fibres.

On the Composition of Certain Subterranean Waters near Port Vendres, and on the Circumstances which Favour this Composition.—Ch. Essner.—The water in question contains free sulphuric acid, and attacks boiler plates to a dangerous extent. They are obtained from rocks containing pyrites and basic iron sulphates.

Researches on the Aromatic Oxyacetones.—P. Crepieux.—This memoir does not admit of useful abstraction.

Reactions of Xylose and Arabinose.—M. Tollens.—Referring to M. Bertrand's communications on the coloured reactions of xylose with orcin and phloroglucine (*Bulletin Soc. Chimique*, v., part 12), the author shows that Bertrand has been anticipated by Whaler, Allen, and Tollens, in the *Annalen der Chemie*, vol. ccliv., p. 314.

MISCELLANEOUS.

Spurious Coffee.—At Lille a manufactory of spurious coffee has been detected, and four of the offenders are in custody. The raw material consisted of the following articles:—15 kilos. chicory, 35 kilos. flour, and 500 grms. iron sulphate—the last mentioned ingredient serving to imitate the natural colour. The lustre of the berries was produced by means of an oil. The plant and materials have been confiscated.—*Chemiker Zeitung*.

The Invertebrata.—Messrs. L. Reeve and Co. have in preparation a volume entitled, "The Physiology of the Invertebrata," by Dr. A. B. Griffiths, F.R.S.E., F.C.S., &c. The book (illustrated with 81 woodcuts) will be of use to physiological chemists, as it treats of the applications of chemistry and physics to the solution of biological problems.

Method of Rendering Portland Cement Unattackable by Frost.—M. Reinhofer.—The object may be effected by the addition of a quantity of soda crystals dissolved in water. The mortar submitted to experiment was composed of 1 litre Portland cement, 1 litre of lime, 3 litres of river sand, mixed with a solution of 1 kilo. soda in 3 litres water. This mortar was exposed for 144 hours to a maximum cold of –31.5°, and was then introduced for three hours into a furnace. When taken out its setting was found quite unaffected.—*Revista di Artiglieria e Genio*.

Alkali-Makers' Pocket-Book.—A new edition, revised and enlarged, of Professor Dr. Lunge and Dr. Hurter's "Alkali-Makers' Pocket-Book" will be issued in a few days in Messrs. Whittaker's Specialist's Series. In this edition numerous small errors in the first edition, almost unavoidable in such a case, have been corrected, some minor improvements have been made, and a considerable number of new methods for analysis have been introduced. The new table of specific gravities of sulphuric, hydrochloric, and nitric acid, and of liquor ammonia, constructed with extreme care, have been substituted for the tables of Kolb and Carius contained in the first edition. As the size of the page has been somewhat increased, the designation "handbook" has been substituted for "pocket-book."

The Chemical Laboratory of Wiesbaden.—In the Summer Term, 1891, there were 74 students on the books. Of these 60 were from Germany, 4 from Russia, 2 from North America, 2 from Spain, 1 from Austria, 1 from Luxemburg, 1 from France, 1 from Sweden, 1 from Bulgaria, and 1 from Australia. Besides the Director, Geh. Hofrath Prof. Dr. R. Fresenius, there are engaged as teachers in the establishment Prof. Dr. H. Fresenius, Prof. Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. G. Frank, and architect T. Brahm. The assistants in the instruction laboratory are 3 in number, in the private laboratory 17, and in the Versuchsstation 3. The next Winter Term begins on the 15th of October. Besides the scientific researches a great number of analyses were undertaken in the different departments of the laboratory and in the Versuchsstation during last term on behalf of manufacture, trade, mining, agriculture, and hygiene.

NOTES AND QUERIES.

Thermo-Chemistry.—Can any of your readers inform me through your paper as to the best and most recent work on Thermo-chemistry, publisher, and price.—C. B.

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Experimental Physics	W. FRESENIUS, Ph.D.
Stoichiometry	E. HINTZ, Ph.D.
Organic Chemistry	Prof. E. BORGSMANN, Ph.D.
Chemical Technology	Prof. H. FRESENIUS, Ph.D.
Microscopy, with exercises in Microscopic work	Prof. E. BORGSMANN, Ph.D.
Chemistry and Analysis of Foods	W. FRESENIUS, Ph.D., and E. HINTZ, Ph.D.
Hygiene	Dr. med. G. FRANK.
Practical exercises in Bacteriology.	J. BRAHM.
Technical Drawing, with exercises	

The next Session commences on the 15th of October. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KRIZDEL'S Verlag, at Wiesbaden, or to the undersigned.

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THE CHEMICAL NEWS.

VOL. LXIV., No. 1661.

THE SPONTANEOUS IGNITION OF COAL.*

By Prof. VIVIAN B. LEWES, Royal Naval College.

THE researches of Grundmann, Fleck, and Richters, on the Continent, have done much towards explaining the somewhat complex phenomena occurring when newly won coal is exposed to atmospheric influences; but in this country little attention has been given to the subject, and with the exception of a report by Sir Frederick Abel, and the late Dr. Percy in 1875, and which is buried in a Blue-book, as far as I know nothing has been published on the subject, with the result that the almost universally accepted explanation of the spontaneous ignition of coal is that it is due to the presence in it of iron pyrites, a theory which I think is entirely erroneous; and my excuse for bringing this paper before you is the enormous importance of the subject to one of the chief coal-producing districts in the kingdom.

The origin and formation of coal has long since been satisfactorily explained, and we know that coal is a fossil fuel of purely vegetable origin, and may look upon it as consisting of three distinct parts:—(1) carbon; (2) hydrocarbons, *i.e.* compounds of hydrogen with carbon, and also with traces of oxygen and nitrogen; and (3) mineral impurities, either derived from the sap of the original plants, which by their checked decay formed the coal-measures, or else which have filtered into the coal during its formation from the surrounding soil.

Of these three factors it is the carbon which forms the bulk of the coal, and which during combustion gives the chief portion of the heat which is evolved, whilst the hydrocarbons, as soon as the coal is heated, escape as gaseous products, and give the fuel the power of burning with flame, and it is upon the proportions in which these principal constituents of the coal are present that the characteristic properties of the various varieties of coal, to a great extent, depend; for instance, in a good Welsh anthracite the percentage of carbon is very high, whilst the amount of volatile hydrocarbons is very low, with the result that the anthracite is hard to kindle and burns almost without flame, whilst a marked contrast to this is a good Cannel, or even Wallsend, coal, in which the percentage of carbon is considerably smaller, but in which the percentage of hydrocarbons is very high, with the result that such coals easily ignite and burn with a considerable amount of flame, or can be utilised for the production of coal gas.

The mineral substances, which are practically the impurities in the coal and mainly form the ash left after combustion, consist of sulphate of lime (gypsum), alumina, silica, and disulphide of iron pyrites, which latter forms the so-called coal brasses found in most seams to a greater or less extent.

Ever since Berzelius first expressed the opinion that the heat given out by the oxidation of iron disulphide into sulphates of iron might have an important bearing on the heating and ignition of coal, it has been adopted as the popular explanation of that phenomenon; and although the work of Dr. Richters clearly proves this not to be the case, the old explanation is still given,—a notable exception, however, being in the case of our great metallurgist, Dr. Percy, who, as early as 1864, pointed out that probably oxidation of the coal had also something to do with spontaneous combustion, a prediction

amply verified by Dr. Richters's researches some six years later.

This disulphide of iron is found in coal in several different forms, sometimes as a dark powder distributed throughout the mass of the coal, and scarcely to be distinguished from coal itself. In larger quantities it is often found forming thin golden-looking layers in the cleavage of the coal, whilst it sometimes occurs as large masses and veins, often an inch to two inches in thickness; but inasmuch as these masses of pyrites are very heavy, they rarely find their way into the screened coal for shipment, many hundreds of tons of these "brasses" being annually picked out from the coal at the pit's mouth and utilised in various manufacturing processes. If the air is dry the pyrites undergo but little change at ordinary temperatures, but in moist air they rapidly oxidise when in a finely divided condition.

It is during this process of oxidation that the heat supposed to cause the ignition is evolved. But when it is considered that some of the coals most prone to spontaneous combustion contain only eight-tenths of a per cent of iron pyrites, and rarely more than 2 per cent, the absurdity of imagining this to be the only cause of ignition becomes manifest. If 100 lbs. of coal were taken, and the whole of the pyrites in it concentrated in one spot, and rapidly oxidised to sulphate, the temperature would barely be raised to 100° C. if all loss of heat could be avoided. Besides which in certain manufactures pure iron pyrites are largely used, and when free from carbonaceous matter may be kept in a state approaching to powder, in heaps containing many hundred tons; and although undergoing continual oxidation, I have been unable to trace a single case of heating, much less a rise of temperature which would approach the igniting point of coal. When, however, it is mixed with finely divided carbonaceous matter, then heating and ignition is a frequent occurrence in even moderate-sized heaps.

I have carefully determined the igniting point of various kinds of coal, and find that—

Cannel coal	ignites at 698° F. = 370° C.
Hartlepool coal	" 766 " = 408 "
Lignite	" 842 " = 450 "
Welsh steam coal	" 870.5 " = 477 "

So that no stretch of imagination could endow the small trace of pyrites scattered through a large mass of coal and undergoing slow oxidation, with the power of reaching the needful temperature.

From these considerations it is evident that we must unhesitatingly discard the old explanation of the cause of spontaneous ignition, and see what other factors we have to deal with.

Carbon, which constitutes so large a proportion of coal, is one of those bodies which possess to an extraordinary degree the power of attracting and condensing gases upon their surface, this power varying with the state of division and density of the particular form used. The charcoal obtained from dense forms of wood, such as box, exhibits this property to a high degree, whilst certain kinds of coal also exhibit the same power, although to a less extent. The absorptive power of newly won coal due to this surface attraction varies, but the least absorbent will take up $1\frac{1}{2}$ times its own volume of oxygen, whilst in some coals more than three times their volume of the gas is absorbed. This absorption is very rapid at first, but gradually decreases, and is, moreover, influenced very much by temperature, for reasons which will be explained later, and this absorption itself causes a rise in temperature which aids the action that is taking place.

The rate of absorption varies with the amount of surface exposed, and therefore able to take part in the condensing action, so that when coal or charcoal is finely powdered, the exposed surface being much greater, absorption becomes more rapid, and rise of temperature at once takes place.

If charcoal is kept for a day after it has been made, out

* Abstract of a Paper read before the British Association, Cardiff Meeting, 1891, Section B.

of contact with air, and is then ground down to a powder, it will frequently fire after exposure to the air for thirty-eight hours; whilst a heap of charcoal powder, of 100 bushels or more, will always ignite. It is for this reason that, in making the charcoal for gunpowder, it is always kept after burning, for three or four days in air-tight cylinders before picking over, and ten days to a fortnight before it is ground.

If newly won coal be at once placed in a measured volume of oxygen, the gas is at first absorbed and its volume diminished; but after it has been in the gas for some little time the coal commences to give off carbon dioxide, and careful investigations show that the oxygen first taken in by the absorptive power of the carbon is now entering into chemical combination with the hydrocarbons of the coal, combining with the hydrogen to produce water, and with the carbon to form carbon dioxide, whilst a small proportion remains in combination in the coal itself, so that the action taking place is of two kinds,—first, absorption of oxygen; and secondly, the setting up of chemical action between the absorbed oxygen and the hydrocarbon.

The absorption of oxygen gives rise to heat, and in the case of coal this rise in temperature all tends to increase the rate of the action which is going on; but it is rarely sufficient to bring about spontaneous ignition, as only about one-third the amount of oxygen being absorbed by the coal,—that is, taken up by the charcoal, and the action being much slower,—tends to prevent the temperature reaching the high ignition point of the coal. Air-dry coal absorbs oxygen more quickly than wet coal. The oxygen so absorbed is in a chemically more active condition than when present in the air, as, in the first place, it is in a condensed condition, and, secondly, is diluted with less nitrogen than in the air, as the carbon absorbs a higher proportion of oxygen than of nitrogen, and this oxygen so absorbed rapidly commences to attack the hydrocarbons present in the coal, having apparently but little action on the carbon itself.

During this action the hydrogen of the hydrocarbons unites with the oxygen to form water, which mostly escapes as vapour, whilst the carbon unites with oxygen to form carbon dioxide or carbonic acid gas, and both these actions result in the generation of heat, which under ordinary circumstances is dissipated to surrounding bodies, but which, when generated in the centre of a mass of fine coal—which, owing to the fact that its interstices are filled with air, is an admirable non-conductor of heat—causes a rise of temperature which in turn increases the rate of action and generation of heat, until a temperature is reached at which the so-called spontaneous ignition ensues.

The most important point to be noticed is the extraordinary effect which initial temperature has on the rapidity of chemical actions of this kind. At a low temperature, and indeed up to about 100° F. = 38° C. the absorption of oxygen, and consequent chemical action, will go on slowly, with practically little or no chance of undue heating taking place; but directly the temperature exceeds 100° F., then, with some classes of coal, ignition is only a question of time and mass.

Although the ignition point of various coals lies above 700° F., yet if many of these coals are powdered, and are placed in perforated zinc cases in masses of 2 lbs. or upwards, and these are kept at a steady temperature of about 250° F. in an oven, ignition will generally follow in a few hours, whilst between this and 150° F. it will take days instead of hours for the same result to follow, and at ordinary English temperatures the mass of broken coal must be very great before much risk of ignition is incurred.

In a paper which I read before the Institution of Naval Architects in 1889 I pointed out that, in the case of coal cargoes, the influence of temperature and mass could be easily traced, and that liability to spontaneous ignition increases with—

1. The increase in the bulk of the cargoes. Evidence given before the Royal Commission of 1875 showed that, in cargoes for shipments to places beyond Europe, the cases reported amount to $\frac{1}{2}$ per cent in cargoes under 500 tons; in cargoes from 500 to 1000, 1 per cent; 1000 to 1500, to 3.5 per cent; 1500 to 2000, to 4.5 per cent; and over 2000 tons, to no less than 9 per cent. Mass influences this action in two ways:—

(a.) The larger the cargo the more non-conducting material will there be between the spot at which heating is taking place and the cooling influence of the outer air.

(b.) The larger the cargo the greater will be the breaking-down action of the impact of coal coming down the shoot upon the portions first loaded into the ship and the larger thereby the fresh surface exposed to the action of the air.

2. The ports to which shipments are made (26,631 shipments to European ports in 1873, resulting in only ten casualties, whilst 4485 shipments to Asia, Africa, and America, gave no less than sixty).—This startling result is partly due to the length of time the cargo is in the vessel, the absorption and oxidation being a comparatively long action; but a far more active cause is the increase of temperature in the tropics, which converts slow action into a rapid one.

3. The kind of coal of which the cargo consists (some coals being specially liable to spontaneous heating and ignition).—There is great diversity of opinion on this point, but it is pretty generally admitted that cases of heating and ignition are more frequent in coals shipped from east coast ports than in South Wales shipments. So much, however, depends upon the quantity of small coal present, that a well-loaded cargo of any coal would be safer than a cargo of Welsh steam coal in which a quantity of dust had been produced during loading.

4. The size of the coal (small coal being much more liable to spontaneous ignition than large).—This is due to the increase of active absorbent surface exposed to the air,—a fact which is verified by the experience of large consumers of coal on land—gas managers recognising the fact that coal which has been stamped down or shaken down during storage is more liable to heat than if it had been more tenderly handled, the extra breakage causing the extra risk.

5. Shipping coal rich in pyrites (or brassea) whilst wet.—The effect of external wetting on coal is to retard at first the absorption of oxygen and so to check the action; but it also increases the rate of oxidation of the pyrites, and they, when oxidised, swell and split the coal into pieces, and this increases heating due to the exposure of fresh dry surfaces, and it is practically only in this way that the presence of pyrites tends to increase the list of spontaneous ignitions.

6. Ventilation of the cargo.—For ventilation to do any good, cool air would have to sweep continuously and freely through every part of the cargo,—a condition impossible to obtain in coal cargoes, whilst anything short of that only increases the danger, ordinary methods of ventilation supplying just about the right amount of air to create the maximum amount of heating. The reason of this is clear. A steam coal absorbs about twice its own volume of oxygen, and takes about ten days to do it under favourable conditions, and it is this oxygen which, in the next phase of the action, enters into chemical combination and causes serious heating. Ventilation, such as used to be sometimes arranged for by a box shaft along the keelson with Venetian lattice upshafts, supplies about as much air as is necessary to produce the results which end in spontaneous ignition.

7. Rise in temperature in steam colliers, due to the introduction of triple expansion engines and high-pressure boilers.—The increase in stokehold temperature due to this is from 5–10° F., and this affects the temperature of the adjacent parts of the vessel.

The same factors which tend to give rise to spontaneous

ignition in coal cargoes will also be found to be the chief causes of ignition in large masses of coal ashore, and the most prolific source of fire in big stores of coal at gas-works, &c., is to be found in ventilating shafts improperly applied, breaking up of the coal, or in some accidental rise in initial temperature, such as a steam-pipe or a boiler in contact with a wall against which the coal is stored.

In the case of coal bunkers in modern steamers and war-ships, the conditions under which the coal is placed are so totally different from those existing in a collier that no comparison can be drawn between them.

In the coal bunker the question of mass, which plays so important a part in a hold laden with coal, is almost entirely eliminated, as 50—400 tons would be about the capacity of any ordinary bunker, and it has been before shown that the cases of spontaneous ignition in masses of coal less than 500 tons does not amount to more than $\frac{1}{2}$ per cent, and the question of initial temperature becomes the most important factor.

A few years ago such an occurrence as a coal bunker on fire was rare, whilst at the present time hardly a week passes without some more or less serious cases occurring on the fast liners, and it is evident that there must exist some well-defined cause for this enormous increase in cases of spontaneous ignition. On collecting evidence on this point, the first thing that strikes one is that bunker fires are almost entirely confined to vessels in which the bunker bulkheads are only separated from the funnel by a narrow air space, or are in close proximity to the boilers themselves, but where the bunkers are stepped back from the funnel casing and boilers, spontaneous ignition is a great rarity.

Taking the case of a fast liner, it is found that the temperature in a coal bunker varies very considerably, according to its proximity to the air channel round the funnel casing. Close to the outside of the bulkhead the temperature is often as high as 200° F. = 93° C., whilst inside 120° would be a fair estimate, and from the centre of the bunker to the side of the vessel it is seldom above 75° F. = 24° C., the temperature, however, being higher nearer the iron decks, which, being in contact with the heated bulkhead, conduct the heat through the coal and raise the temperature often up to 100° F.

It has been pointed out that if coal is kept at a high temperature, even though it be far below its igniting point, ignition is only a question of time, and if the bunker coal next the bulkhead is kept at 120° F. any coal with a tendency to absorb oxygen will run a great chance of igniting within a few days. It is manifest that if this is the real cause of ignition, the seat of the fire ought to be found close to the heated bulkhead, but this is very often not the case, the mass of fire being found near the centre of the bunker, and sometimes even towards the side of the vessel; but careful examination soon reveals the cause of this, as a line of charred coal is mostly to be found running from the heated bulkhead to the seat of active combustion, showing that the fire started by the high initial temperature has not had sufficient air near the bulkhead to do more than smoulder, but that as soon as it came in contact with a current of air passing up through the coal from the hatches in the decks the smouldering mass began to burn fiercely.

The tendency to spontaneous ignition in coal has always been supposed to increase with the quantity of pyrites present in it, but experiment shows that it is the tendency or power of the coal to absorb oxygen which must be taken as the true index of danger, and this may be roughly gauged by the amount of moisture which the coal has absorbed from the air, as if much moisture be found in an air-dried sample of coal it at once stamps it as a highly-absorbent form, and which must on that account be stored with special precautions, whilst if but little moisture be present it is probably unable to take up enough oxygen to lead to serious mischief.

This is very beautifully shown in a table compiled, I

believe, by Dr. Percy, which also makes it clear how little the pyrites have to do with ignition:—

	Liability to spontaneous combustion.	Pyrites p.c.	Moisture p.c.
Very slight		1.13	2.54
		1.01 to 3.04	2.75
		1.51	3.90
Medium		1.20	4.50
		1.08	4.55
		1.15	4.75
Great		1.12	4.85
		0.83	5.30
		0.84	5.52
		1.00	9.01

When once a coal has taken up oxygen, and the early stages of heating are passed and the temperature has again fallen, all danger of ignition is over, and it may be stored in any quantity with perfect safety, so that if it were practical to keep newly-won coal for a month in moderate sized heaps, and then to avoid much breakage in afterwards loading it, spontaneous ignition would be almost unknown.

NOTE ON THE ELECTROLYSIS OF ALLOYS.*

By HENRY C. JENKINS, Assoc.M.Inst.C.E., F.C.S.

THE importance of the question as to whether alloys are capable of being electrolysed has for a long time been recognised, and has already been under the notice of a Committee of this Association. Several experimenters have endeavoured to separate the constituents of some alloys by such means, but hitherto no success in this direction has been recorded.

Doubtless one reason for this negative result may be found in the difficulty of submitting a metallic bath to a sufficiently large difference of potential, owing to its very low resistance, but from the same cause there is another reason why electrolysis should not take place, at least in the case of the majority of alloys, to which prominence does not hitherto seem to have been given.

The variable polarisation, and the resistance of electrolytic baths generally, have led to the adoption of the view that, in an electrolytic bath, the electricity is conveyed by some method of convection, or of successive molecular discharge; streams or chains of molecules carrying electrical charges from one electrode to the other. The bath itself is formed of some body whose resistance when pure is extremely high, so that it is necessary in general to add another body to it—an impurity—which probably acts by increasing the number of free molecules present. It is easy to imagine that in such an insulating medium molecules can be charged with electricity, which charge they can retain until they reach some body having a different potential. But free molecules could not retain a charge if entirely within a conducting envelope and in contact with it, and although the possibility of the possession of a gaseous envelope by the molecules in a liquid has been recognised, still the conductivity of pure molten metals is scarcely in favour of any view that there is actual insulation between their molecules, and if there were any considerable insulation of this kind, it is difficult to account for the effect upon electrolytes of very small electromotive forces. It will thus be seen that the want of success in the attempts to electrolyse molten alloys still leaves quite open the question of their constitution, whilst it is in full accordance with Laplace's equation of electrical potential.

From the fact, however, that alloys in many cases form

* A Paper read before the British Association, Cardiff Meeting, 1891, Section B.

true compounds, which may be obtained in a crystalline form if proper conditions are chosen, and because the conditions as to temperature of an electrolytic bath may be those most favourable to the precipitation of such a compound out of solution, it follows that all future electrolytic experiments with alloys should be made at temperatures sufficiently high to fuse any possible compound, otherwise very deceptive results would be obtained, owing to the difficulty of correctly sampling the bath.

PRELIMINARY NOTE ON TRAUBE'S TETROXIDE OF SULPHUR.

By DOUGLAS CARNEGIE, M.A.

In the current number of the *Berichte* (June 8) Traube, in a paper on the so-called persulphuric acid (obtained by electrolysis 40 per cent solutions of sulphuric acid), quotes analyses which in his opinion prove that this substance is not S_2O_7 , as its discoverer (Berthelot) supposed, but that it is in reality the radicle sulphion SO_4 .

Although the author sees no theoretical objection to the existence of a peroxide of sulphur of the composition SO_4 , yet he does not think that Traube's analyses are such as to warrant a dogmatic assertion to the effect that such an oxide is known and realisable.

It is the object of this paper to criticise Traube's methods and conclusions.

In the first place it should be noted that Traube did not succeed in isolating his alleged SO_4 . His conclusions are founded on analyses of solutions of the peroxide of sulphur in (I.) H_2SO_4 Aq. and (II.) K_2SO_4 Aq.

I. A portion of the persulphuric acid solution was treated with excess of ferrous sulphate, and then the excess of ferrous iron titrated with permanganate. In this way the "active" oxygen of the peroxide was determined. From another portion of the boiled acid solution $BaSO_4$ was precipitated, by means of HCl Aq. and $BaCl_2$ Aq. The weight of this precipitate gave the amount of SO_3 resulting from the complete decomposition of the peroxide.

TABLE I.

Active O found.	$BaSO_4$ found.	SO_3 calculated.	Ratio O : SO_3 .
9.62 m.g.	144 m.g.	49.5 m.g.	1 : 5.14

Theory for SO_4 — SO_3 : O :: 5 : 1.
 " S_2O_7 — SO_3 : O :: 10 : 1.

From a comparison of the theoretical and experimental numbers Traube concludes, firstly, that Berthelot's oxide cannot be S_2O_7 ; and secondly, that it must have the composition SO_4 . (It may be noted, in passing, that in spite of the speciousness of the ratio 1 : 5.14 the experimental results nevertheless involve an error of 2.8 per cent, if Traube's views be correct.)

While admitting the justness and necessity of the first conclusion, I nevertheless hesitate to accept the second, and for the following reasons:—Moissan, from determinations of total hydrogen and active oxygen, concludes that the so-called perchromic acid has the empiric formula $CrO_3 \cdot H_2O_2$. From certain considerations founded on the formula for hydrogen peroxide, taken in conjunction with Mendeleeff's "principle of substitution," it would, however, seem better to double Moissan's empiric formula, and write it in the form $Cr_2O_7 \cdot H_2O_2 \cdot H_2O$. Such a formula is supported by the well-known fact that peroxides (as defined by Mendeleeff, *Berichte*, xv., 242) possess a remarkable power of combining with H_2O_2 to form fairly stable compounds. Whether or not Fairley's peruranates will, on the more detailed investigation which they undoubtedly deserve, turn out to be similar derivatives of the oxide U_2O_7 , as Mendeleeff suggested in his Faraday lecture, remains to be seen. Quite recently compounds

of the peroxide form M_2O_7 (where $M = W$ and Mo) have been described, so it would seem that all the members of the sulphur group—as group is understood in connexion with the periodic law—form oxides of the type M_2O_7 .

Now there is nothing whatever in Traube's analyses to show that he was not working with the very probable compound $S_2O_7 \cdot H_2O_2 \cdot H_2O$, which would on decomposition furnish SO_3 and active O in the proportion 5 : 1. As a matter of fact the conditions observed in the preparation of Berthelot's oxide would be favourable to the production of hydrogen peroxide, and, moreover, Traube himself states that the sulphur oxide under discussion is decomposed by pure water, with formation of hydrogen peroxide and evolution of oxygen.

It cannot, however, be claimed that this reaction of the peroxide with water has much weight as an argument for the proposed formula $S_2O_7 \cdot H_2O_2$. For that anomaly, potassium peroxide, K_2O_2 , is said to be decomposed by water, with production of hydrogen peroxide and oxygen.

II. The primarily obtained solution of sulphur peroxide in electrolysed H_2SO_4 was exactly neutralised by KOH Aq. Thus there resulted a solution of the peroxide (itself wholly destitute of acidic properties) in neutral K_2SO_4 Aq.

The active oxygen in a portion of this neutral solution was determined ferrometrically as in I., and also iodometrically. Another portion of the solution having been boiled, the SO_3 resulting from the decomposition of the alleged SO_4 was determined by standard alkali. In this way the following numbers were obtained:—

TABLE II.

Active Oxygen determined Ferrometrically.	Active Oxygen determined Iodometrically.	SO_3 determined Acidimetrically.	Oxygen (Iodometric): SO_3 .
M.grms.	M.grms.	M.grms.	
8.40	7.28	36.4	1 : 5.00
6.06	5.04	23.0	1 : 4.56
16.20	12.00	56.2	1 : 4.70
27.15	21.28	110.3	1 : 5.10
32.00	24.00	117.0	1 : 4.89

Mean 1 : 4.85

It will be noticed that the iodometric determinations of active oxygen always fall below the ferrometric ones. Traube advances the following explanation:—The potash used to neutralise the solvent H_2SO_4 contained carbonated alkali; hence the resulting neutral solution would contain, besides the peroxide and K_2SO_4 , considerable quantities of potassium bicarbonate. This bicarbonate, Traube asserts, would react with an equivalent quantity of the iodine set free, and so vitiate the final thiosulphate titration. Even admitting what seems improbable, viz., that the neutralised solution contained considerable quantities of $KHCO_3$, can we further permit ourselves to agree with Traube in his assertion that bicarbonate fixes an equivalent quantity of iodine? Fresenius, in his "Quantitative Analysis," quotes special experiments showing that aqueous solutions of the bicarbonated alkalis are practically without action on iodine.

According to Traube the presence of this bicarbonate also vitiates the SO_3 determinations, but in such a way that the error tends to compensate that made in the iodometric determinations. Hence the ratio O : SO_3 is unaffected by the double error.

We find ourselves unable to appreciate the portion of Traube's paper following the above discussion of the iodometric error. Suppose the ratio $\frac{a}{b}$ to have a certain value, K, and let x be any quantity. Then it is obvious mathematically that the ratio—

$$\frac{a+x}{b+\frac{x}{K}}$$

will have the value K. Nevertheless Traube would see in this numerical discovery a strong confirmation of the existence of the compound SO_4 .

Final experiments are then described which do away with the disturbing influences supposed to be caused by the presence of bicarbonates. At the same time these experiments render possible the direct determination of the ratio $\text{SO}_3 : \text{O}$ determined ferrometrically. I have supplemented the results given in Table III. by a column of percentage errors.

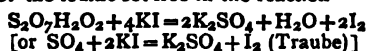
TABLE III.

Active Oxygen determined Ferrometrically.	SO_3 .	$\text{O} : \text{SO}_3$.	Percentage Errors.
22.54 m.grm.	96.3 m.grm.	1 : 4.3	14.5
23.90 "	108.6 "	1 : 4.5	9.2

Errors of 14.5 and 9.2 per cent do not appear to embarrass the ardent seeker after SO_4 . Traube, commenting on the above results, concludes—"Here also the ratio of both decomposition products is nearly 1 : 5 (sic). There is no doubt but that an indifferent body of the composition SO_4 exists."

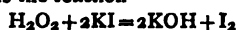
In a previous paper which appeared in this Journal I showed that the unreliability of Duflos's method of estimating ferric salts is referable to the impurity of ordinary samples of "pure" KI, which salt invariably contains more or less free alkali. To the same source I would in part refer the discrepancies between the iodometric and ferrometric oxygen determinations alluded to.

Some of the iodine set free in the reaction—



reacts at once with an equivalent of the potash presumably contained as impurity in the potassium iodide used, and vitiates the results. Hence it is reasonable to suppose that the iodometric method would give true values for the active oxygen were acid, instead of neutral, solutions of the peroxide employed. In a footnote Traube asserts that this is actually the case.

It has previously been remarked that the conditions observed in the preparation of sulphur peroxide are eminently favourable to the production of H_2O_2 . It may be that more of this substance is formed than is necessary to combine with the S_2O_7 produced to form $\text{S}_2\text{O}_7\text{H}_2\text{O}_2$; at any rate the low ratio $\text{O} : \text{SO}_3$, found in the majority of Traube's analyses seems to demand some explanation other than mere experimental error. Moreover, in neutral solutions the reaction—



would not take place quantitatively, and herein one may seek for a further explanation of the discrepancies between the iodometric and ferrometric determinations of active oxygen, and of the fact apparent in Table II., that the iodometric error increases *pari passu* with the quantity of peroxide analysed.

The greatest discrepancy between the ferrometric and iodometric oxygen determinations quoted in Table II. amounts to 8 m.grms. oxygen. It is easy to see that 56 m.grms. of free alkali in the KI used would produce an error of this magnitude. If 3 grms., say, of potassium iodide were used in the volumetric determination, a potash impurity of less than 2 per cent—by no means an excessive quantity—would fully account for their regularities noticed.

The foregoing criticism of Traube's work suggests several experiments on the peroxide of sulphur, and these I hope to carry out and communicate shortly.

Boulder, Colorado

Intermittent Mercurial Air-Pump. — K. Prytz (*Annalen der Physik*).—A wide U-tube with limbs of unequal length. If mercury is let fall with a certain speed into the longer limb, a certain quantity of mercury is each time expelled from the oblique end of the shorter limb into the descending tube.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 150.)

XLII.—Tantalum.

1. SALTS of potassium produce in solutions of tantalic and hydrofluoric acids the separation of thin prismatic crystals of the sparingly soluble salt K_2TaF_7 , whilst fluoxyniobate, which is formed simultaneously, remains in solution. The prisms of potassium fluotantalate resemble crystals of gypsum; their length amounts to 50—100 micro. The limit of the reaction is at 0.006 m.grm. Ta.

The required solution is most simply obtained by melting tantaliferous minerals with sodium and ammonium fluoride. It is dissolved in hot water with the addition of a little hydrochloric acid. It is preferable first to separate out a mixture of tantalic and niobic acids by fusion with potassium bisulphate and extraction with hot water, and to bring this into solution by heating with water and ammonium fluoride, adding finally a little hydrochloric acid. For a tolerably complete precipitation of tantalum, at least ten minutes must be allowed after the addition of the potassium chloride.

2. Soda-lye precipitates from alkaline solutions of tantalic acid the salt $\text{Na}_4\text{Ta}_2\text{O}_{10} + 25\text{H}_2\text{O}$ in hexagonal tablets and stars measuring 30—50 micro. They are colourless, and otherwise they resemble the crystals of sodium silico-fluoride. At the beginning of the crystallisation there appear also rods and needles which can scarcely be distinguished from crystals of sodium niobate. On this account the reaction 1 deserves the preference. The limit is at 0.0012 m.grm. Ta.

XLIII.—Bismuth.

1. Oxalic acid throws down from solutions of bismuth a heavy, pulverulent white precipitate. The precipitation is effected more rapidly and completely by means of potassium bioxalate. If heated in the acid liquid bismuth oxalate crystallises in pyramids of a quadratic section which refract light strongly and are from 6—15 micro. in size. The limit of this reaction which ensues decidedly at a dilution of 1000 times is at 0.0003 m.grm. Bi.

2. Rubidium chloride and caesium chloride yield with compounds of bismuth dissolved in hydrochloric acid, hexagonal tables probably belonging to the rhombic system, which are 300 micro. in size with rubidium chloride and 100 micro. with caesium chloride. They are thin, but have a well-defined outline and polarise strongly. If tin is present bismuth falls subsequently in prismatic crystals extended in length. For solutions which contain less than 0.2 per cent of bismuth nitrate, caesium chloride is preferable as a reagent. An addition of potassium iodide retards the reaction and makes the crystals smaller. They appear as ridges, rhombs, and hexagons, varying from the colour of red lead to blood red. This reaction, which attaches itself conveniently to the examination of tin, indicates 0.00013 m.grm. Bi.

3. Potassium sulphate (or preferably bisulphate), yields colourless discs in solutions of bismuth if not too dilute (compare Potassium 3). They are more easily found than the small pyramids of reaction 1, but the reaction with potassium sulphate requires solutions which contain at least 0.2 per cent of bismuth nitrate. Limit of the reaction 0.0003 m.grm. Bi.

4. The precipitation of bismuth nitrate or chloride by water cannot be recommended for micro-chemical research. Much more striking phenomena are obtained by an addition of potassium iodide. From a hydrochloric solution water precipitates bismuth iodide with a blackish brown colour, which turns to a reddish brown on heating;

* Zeit. Anal. Chemis.

in presence of lead it is scarlet, of antimony dark red, and of tin orange-red. Limit of the reaction 0.0004 m.grm. Bi.

XLIV.—Antimony.

1. In solutions of antimony chloride in dilute hydrochloric acid caesium chloride produces crystals of about 80 micro. very similar to those described under Bismuth.
2. Rubidium chloride yields crystalline leaflets of 300 micro. paler than those of chlorobismuthite. If potassium iodide is added along with caesium chloride, the sensitiveness of the reaction is doubled, and we obtain crystalline leaflets of a bright orange, the colour of which may be recognised along with bismuth, as iodostibite crystallises after iodobismuthite. The limit of the reaction is at 0.00008 m.grm. Sb.

2. Oxalic acid converts antimony oxychloride into antimonyoxalate. This compound is precipitated from slightly acid solutions of antimony by potassium bioxalate. It appears in translucent brownish tufts and pencils composed of very fine fibres. The oxalate dissolves in hydrochloric acid, but water re-precipitates it unaltered. These reactions may be masked by tin, bismuth, and lead. The limit is at 0.001 m.grm. Sb.

3. Barium tartrate with a slight addition of barium chloride dissolves at a boiling heat antimony hydroxide and oxychloride. Whilst cooling there are formed the crystalline leaflets of barium stibiotartrate described under Barium 4. If the antimony is previously eliminated as sulphide, as Streng recommends, the reaction is trustworthy and characteristic. It is then, however, more tedious than 1, and is about equal in sensitiveness to 2.

4. Precipitation as sodium antimoniate gives better results for antimony than for sodium. The specimen is melted with 5 vols. of saltpetre until about the half is driven off, dissolved in hot water, and to the clear solution there is added a granule of sodium chloride. The crystals obtained are chiefly lenticular, of 20–25 micro., often grouped in triplets, and intersecting each other according to the axes of an octahedron. Between them there occur little rods which might be taken for crystals of sodium niobate. The limit of this reaction is at 0.0005 m.grm. Sb. Hitherto it is the only available reaction for antimonious acid.

XLV.—Arsenic.

(a) Arsenious Acid.

1. Nitric acid produces no precipitate in a solution of arsenic trioxide in potassa-lye unless highly concentrated. Evaporation at a gentle heat determines the separation of arsenious acid in small, distinct octahedra, the number and size of which increase whilst the liquid cools. They measure 8–15 micro., and refract light strongly and are colourless. Hydrogen sulphide turns them slowly yellow. The limit of the reaction is at 0.0002 m.grm., $As_2O_3 = 0.00014$ m.grm. As.

(b) Arsenic Acid.

1. With the salts of calcium we obtain, by the same process as for the precipitation of ammonium magnesium phosphate, hemimorphous crystals of the rhombic system, up to 60 micro., and of the same appearance as those of the salt above mentioned.

From very dilute solutions we obtain chiefly small rods of 15 micro., in which the hemimorphic structures can scarcely be recognised. The limit of this very characteristic and sensitive reaction is 0.000035 m.grm. As.

The oxidation of arsenical compounds to arsenic pentoxide is best effected by gently heating along with hydrochloric acid and potassium chlorate. For the reaction just described it must be remembered that ammonium chloride dissolves perceptible quantities of ammonium-calcium arseniate. Arsenic acid forms analogous sparingly soluble double salts with zinc, cadmium, and copper, but not with strontium, barium, and lead.

2. Ammonium molybdate precipitates solutions of arseniates in dilute nitric acid at the ordinary temperature, but only after the lapse of some time. Heat acceler-

ates the precipitation remarkably. The precipitate is perfectly similar to the ammonium phosphomolybdate. Limit of the reaction 0.00022 m.grm. As.

In all cases where supersaturation with ammonia is admissible, the preference must be given to reaction 1, which leaves no room for confounding arsenic and phosphorus. Besides, the reaction with molybdate admits of mistakes with vanadium and bismuth, and if much ammonium chloride is present in solution with silicon. Compare silicon and rubidium.

(To be continued).

NEW METHOD OF DETERMINING CHROME YELLOWS.

By MM. LACHAUD and C. LEPIERRE.

OUR researches on chromates have led us to propose a new process for the determination of lead chromate in the chrome yellows of commerce. Lead chromate, in contact with dilute solutions of potassa, is split up according to the equation—



If we precipitate the potassium solution by a strong and concentrated acid, the inverse reaction is produced and the lead chromate is regenerated. On the contrary, under certain conditions, the determination of the potassa which remains free in contact with basic chromate (which is almost insoluble if we operate in the cold and in a dilute liquid), furnishes a rapid process for the determination of lead chromates. According to the above equation 1 mol. lead chromate (323) corresponds to 1 mol. potassium hydrate (56), or 1 part of chromate to 0.17337 potassa.

We proceed as follows:—We weigh accurately 2 grms. lead chromate and prepare two solutions, one of binormal potassa (112 grms. KOH per litre); this potassa neutralises exactly a solution of sulphuric acid at 1 mol.-gram. per litre (98 grms.). The chromate is placed in a flask with a ground glass stopper, and there are added 20 c.c. of the standard potassa. It is shaken strongly until the yellow granules of the chromate disappear, and basic chromate occupies the bottom of the flask. The liquid is diluted with distilled water; it is decanted and filtered to separate the basic chromate. The excess of potassa is neutralised with the standard sulphuric acid, using phenol phthalein as indicator. To render the process capable of determining the impurities in the chromates down to less than 1 per cent (which is sufficient in practice), we neutralise the larger part of the potassa with a certain volume of the binormal sulphuric acid, and we complete the titration with a solution of exactly the strength of this binormal solution; with 2 grms. of chromate and 20 c.c. of potassa, we add to the dilute liquid immediately 16 c.c. of binormal SO_4H_2 . An excess of potassa is necessary to attack the chromate, for this renders the operation more rapid. If the solutions are ready prepared, and without counting the time of weighing, a chromate may be determined in ten minutes; this lapse of time is much less than that required by other volumetric methods.

But we may dispense with the filtration if many determinations have to be effected by making a small correction (scarcely 0.1 in 20 c.m.c.), due to the action of acid solutions upon the basic chromate. To render the operation more rapid by dispensing with calculations, we use a solution of potassa such that 0.1 c.m.c. corresponds to 1 per cent of pure lead chromate. For this purpose it is sufficient to prepare either with the normal solution or directly a potassic liquid containing 17.337 grms. of KOH in a litre of water, and to prepare a sulphuric solution neutralising it exactly; 1 litre of these two solutions corresponds to 100 grms. of pure chromate.

We weigh 2 grms. of chromate, and operate upon 40 c.c. of the potassa solution. If the chromate is pure, 20 c.c. of sulphuric acid are required to neutralise the potassa. If the chromate contains 50 per cent of impurities, 30 c.c. are required, &c.—*Bulletin de la Soc. Chimique de Paris.*

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1891.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, *Metropolis Water Act*, 1871.

London, September 9th, 1891.

SIR,—We submit herewith the results of our analyses of the 174 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from August 1st to August 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 174 samples examined, the whole were found to be clear, bright, and efficiently filtered, excepting three, which were recorded as "very slightly turbid."

Throughout the month of August, notwithstanding the excessive and often stormy rainfall, the character of the water-supply to the Metropolis continued to be eminently satisfactory. The extreme degree of freedom from organic matter which characterised the supply of the previous month was fully maintained; and the effect of the storm-rainfall was noticeable only in a slightly diminished degree of freedom from colour-tint, and in the occurrence of the three samples of water noted as "very slightly turbid." The maximum amount of organic carbon present in any single sample examined was only 0.128 in 100,000 parts of the water, corresponding to considerably under a quarter of a grain of organic matter per gallon. A comparison of the results afforded by the Thames-derived supply in the months of July and August respectively, with the mean results afforded by the previous four months' supply, is shown in the following table:—

	Ratio of brown to blue tint.	Oxygen re- quired for oxidation.	Organic carbon per 100,000	Organic carbon per 100,000
	Means.	Means.	Means.	Maxima.
<i>Thames supply:—</i>				
Mean of pre- vious four months ..	13.0 : 20	0.051	0.147	0.209
July ..	8.9 : 20	0.046	0.121	0.142
August ..	11.4 : 20	0.045	0.114	0.128

We are, Sir,

Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

NOTE ON THE

COMPOSITION OF THE ASH OF THE ACHYRANTHES ASPERA, LINN.

By C. J. H. WARDEN,
Chemical Examiner to the Government of Bengal.

THE *Achyranthes aspera*—"prickly chaff flower"—occurs in India as a weed in gardens, and is found all over the country. In Sanskrit the plant is called Apamārga, or the *washerman*, on account of the large quantity of alkali contained in its ash, which is utilised by native washermen in certain parts of India, and which is also used as an alkali in dyeing and in the preparation of alkaline medicines and caustic pastes.*

The plants used for the following ash determinations were collected in Alipore, Calcutta, in August. The leaves, stems, and roots, dried at 100° C., afforded respectively the following percentages of ash:—Leaves 24.334, stems 8.672, roots 8.863.

The ash had the following percentage composition:—

	Leaves.	Stems.	Roots.
P ₂ O ₅	3.0257	2.6939	1.8594
SiO ₂ as sand	39.7192	12.9716	21.4219
SO ₃	1.3200	2.0534	3.9523
CaO	13.8893	13.1233	12.9335
MgO	3.4778	3.5149	5.4419
K ₂ O	17.8454	32.0008	28.5830
Na ₂ O	—	—	0.9860
Fe ₂ O ₃	2.7931	3.0352	5.6297
Manganese (traces) ..	Not estimated.	Not estimated.	Not estimated.
KCl	5.7416	9.5221	—
NaCl	1.1770	1.5261	3.2951
Al ₂ O ₃	2.0651	Not estimated.	Not estimated.
CO ₂	8.8687	13.6294	11.0057
Charcoal	0.3297	0.5525	Not estimated.
	100.2526	95.2232	95.1085

The large amount of sand present in the ash was due to the plants having been collected during the "rains," and when received they were coated with finely-divided silicious matter—especially the leaves—which it was impossible to wholly separate. The total potash, if calculated as K₂O, would be equivalent in the leaves to 21.4986 per cent, in the stems to 38.0122 per cent, and in the roots to 28.5830 per cent. It is possible that the plant might be of value as a cheap "green manure" on account of its potash content. Compared with worm-wood and fumitory wood, which, according to Hörs' analyses, afford respectively 9.74 and 21.9 per cent of ash, containing 74.94 and 36.48 per cent K₂O, the ash of the *Achyranthes aspera* is fairly rich in potash.

Medical College, Calcutta.

EXAMINATION OF MANURES, CATTLE-FOODS, AND SOILS.†

EXAMINATION OF ARTIFICIAL MANURES.

A.—The Preparation of the Samples in the Laboratory, and General Determinations.

1. DRY samples of phosphates or other artificial manures may be sifted and then mixed.
2. In moist manures, in which this cannot be effected, the preparation is confined to a careful intermixture.
3. On the arrival of the samples their weight is ascertained. One half of the sample is prepared for analysis,

* Dymock, "Materia Medica of Western India."

† *Zeitschrift für Analytische Chemie.*

and the other, up to 1 kilo. in weight, is preserved in tightly-closed glass bottles in a cool place for a quarter of a year, reckoning from the day of despatching the report of the analysis, unless some other arrangement has been agreed on with the party sending the sample in question.

4. In crude phosphates and animal charcoal the moisture is determined at 105–110°, as a proof of identity. In samples which, during desiccation, may lose ammonia in any form whatever, this must also be determined.

5. Only average samples, carefully taken, and of at least 250–500 grms. and packed in well-fitting glass bottles, should be sent for analysis.

6. The weight of the samples sent in should be stated on the certificates of analysis.

7. In substances the moisture of which varies on pulverising the proportion of water must be determined both in the powdered and in the rough state, and the result of the analysis should be calculated according to the moisture of the original rough substance.

B.—Examination of Phosphatic Manures.

1. The extraction of superphosphates is effected by placing 20 grms. of the sample in a litre flask, pouring upon it 800 c.c. of water, and shaking it strongly and continually for half an hour, for which purpose a special machine has been invented, and may be set in action by hand or by any motor. About 150 rotations per minute are recommended. The flask is then filled up to the mark with water, the total liquid well shaken up and filtered. This process was introduced in the laboratories of the Association of Agricultural Experimental Stations on January 1st, 1891.

2. The solutions of double superphosphates must be boiled with nitric acid before the precipitation of the phosphoric acid, in order to convert any pyrophosphoric acid present into the tribasic acid. To 25 c.c. solution of superphosphate, 10 c.c. of concentrated nitric acid (1·4 specific gravity) are to be used.

3. In arbitration analyses the molybdenum method is to be used. The comparative determinations of superphosphate by the citrate method and the molybdenum methods as instigated by the commission must be made known at the next general assembly.

4. For determining the iron and alumina in crude phosphates the method of Glaser is for the present accepted as decisive:—5 grms. phosphate are dissolved in the known manner in 25 c.c. nitric acid of specific gravity 1·2, and in about 12·5 c.c. of hydrochloric acid of specific gravity 1·12, and made up to 500 c.c. 100 c.c. of filtrate, representing 1 gm. of the original substance, are placed in a $\frac{1}{2}$ -litre flask, and 25 c.c. sulphuric acid of specific gravity 1·84 are added.

The flask is let stand for about 5 minutes and shaken for a few times, adding then 100 c.c. alcohol at 95 per cent, and cooling the flask, which is then filled up to the mark with alcohol and well shaken, when contraction takes place. The stopper is lifted, the flask again filled up to the mark with alcohol, and shaken again. After standing for half an hour it is filtered. 100 c.c. of the filtrate, representing 0·4 gm. of the original substance, are evaporated down in a platinum dish until the alcohol is expelled. The liquid, free from alcohol, is mixed with about 50 c.c. of water in a beaker and heated to boiling. Ammonia is then added until the reaction is alkaline, but not during the boiling, to avoid a violent effervescence.

The excess of ammonia is driven off by boiling. The liquid is let cool, filtered, the precipitate washed with hot water, ignited, and weighed as ferric phosphate plus aluminium phosphate; half the weight found is assumed as consisting of $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$. By this method the determination can be effected in from 14–2 hours.

5. The fine meal in basic slag meals is determined according to the method agreed on at Bonn. The operation is as follows:—50 grms. ground slag are placed in a sieve with a surface of not less than 20 c.m. in diameter, and made of the wire tissue, No. 100, by Amandus Kahl,

of Hamburg (smooth texture), and shaken for fifteen minutes by hand or in a suitable machine.

6. For determining the moisture in superphosphates 10 grms. of the sample are heated to 100° for three hours; the loss of weight is assumed as water.

7. For determining phosphoric acid in bone-meal, fish guano, meat manure, and crude phosphates, as also total phosphoric acid in superphosphates, 5 grms. are dissolved in 50 c.c. aqua regia, consisting of 3 parts hydrochloric acid of specific gravity 1·12, and 1 part nitric acid of specific gravity 1·25, or it is boiled with 20 c.c. nitric acid of specific gravity 1·42 and 50 c.c. sulphuric acid of specific gravity 1·8 for half an hour.

C.—Examination of Nitrogenous Manurial Substances.

1. Nitrogen in the form of blood, flesh-meal, and similar organic matters, can be determined either by the Kjeldahl's process or with soda-lime.

2. Nitric nitrogen in mixtures may be determined according to Schlösing, Grandeau, or Lunge. Total nitrogen is determined according to the Kjeldahl-Jodlbauer or some similar process.

In Peruvian guano, whether crude or rendered soluble, the nitrogen, on account of the nitrates present must be determined by the Kjeldahl-Jodlbauer or by some analogous method.

3. For the determination of nitrogen in saltpetre a direct method should be sought for.

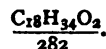
4. The total nitrogen in commercial ammonium salts should be determined by distillation with soda-lye.

Examination of Cattle-Foods.

The extraction of fats, which ought to be complete, is effected exclusively by means of ether free from alcohol and water. The weighed ethereal extract should dissolve in anhydrous ether without residue.

The commission is requested to explain the determination of fat in linseed cake by further experiments.

It was resolved to institute experiments concerning the degree of acidity of the extracted fat. It was recommended to use phenol-phthalein as indicator, and decinormal soda-lye as standard solution, as proposed by H. Fresenius, and to calculate the results as oleic acid—



1 c.c. decinormal lye = 0·0282 gm. oleic acid. It was recommended to throw further light upon the value of the "iodine number" for the analysis of foods by its more frequent determination.

It was resolved to express the proportionate money-value of proteins, fat, carbohydrates, by 3 : 2 : 1.

(To be concluded).

ON THE DETERMINATION OF NITRATES IN WATER.*

By ALLEN HAZEN and HARRY W. CLARK.

(Concluded from p. 122).

II. Aluminum Process.

As usually described (Sutton's "Volumetric Analysis," Fifth Edition, p. 364), the aluminum process for the determination of nitrates consists of boiling a portion of the water with caustic soda, to expel ammonia, and after cooling, adding a piece of aluminum foil. The hydrogen evolved reduces the nitrates and nitrites present to ammonia. The hydrogen is taken through dilute acid to hold any ammonia that may be given off. After reduction is complete, the acid is washed into the water, and the ammonia distilled and nesslerised.

* *Journal of Analytical and Applied Chemistry*, June, 1892.

The process may be divided into two parts: the reduction to ammonia, and the estimation of the ammonia formed. For convenience we shall first consider the determination of the ammonia, and afterwards the conditions of complete reduction.

The amount of ammonia removed by the hydrogen is ordinarily so small that it seemed better to estimate its quantity and apply a correction, rather than use the troublesome absorption tubes of glass moistened with acid. The proportion of ammonia removed depends upon temperature and the amount of aluminum dissolved. Fifty c.c. of water saturated with ammonia at 20 degrees holds 26 grms. If the water contains 0.001 gm. of ammonia it is 1-26,000 saturated. One gm. of aluminum in dissolving gives off 1200 c.c. of hydrogen, and, supposing the ammonia to obey exactly the laws of gases, this should carry 1-26,000 of its volume of ammonia, or 0.046 c.c., weighing 0.000035 gm. or 3.5 per cent of the whole amount of ammonia present. With different amounts of aluminum, and the same volume of water, the loss is directly proportional to it, being 1.75 per cent when $\frac{1}{4}$ gm. is dissolved. With different amounts of ammonia, the same percentage is removed. At higher temperatures the loss is greater, becoming 4.6 per cent at 30 degrees for 1 gm. of aluminum in 50 c.c. With reduced pressure the loss is greater, and is inversely proportional to the pressure. The loss from a nitrate solution is slightly less than from an ammonia solution, because there is no ammonia to be lost when the first hydrogen is given off.

Numerous experiments, keeping the acid separate from the bulk of the water, show that the above estimates are slightly above the truth, but they form a satisfactory basis for corrections, which practically never exceed 2 per cent.

We have found that, with ground waters at least, distillation of the ammonia after reduction is unnecessary, quite as good results being obtained by diluting an aliquot portion and nesslerising direct. The conditions of success of this process are that the water after reduction shall be practically colourless, and free from the black residue of the aluminum, and that no alumina shall precipitate before nesslerisation. The reducing action of the nascent hydrogen, with the caustic alkali and the carbonate always present, clarifies a majority of waters sufficiently, and it is only with the yellow swamp waters with low nitrates, where large volumes must be taken for the determination, that the colour interferes with the result. Waters usually settle so clear after the action that suspended matters are not troublesome. The separation of alumina causes the greatest difficulty, clouding the tube, and often seriously lowering the readings. This can be prevented by using for dilution distilled water entirely free from carbonic acid. Such water can be easily prepared by blowing steam through ordinary good distilled water. This treatment will also remove every trace of ammonia. Care

must also be taken that the carbonic acid of the breath does not come in contact with the water while measuring with a pipette.

When the aluminum-mercury couple suggested by Ormandy and Cowhen* is used, direct nesslerisation cannot be applied, for the separated alumina invariably holds a portion of the ammonia, and the results are too low. With caustic soda, however, at the end of the reaction, everything is in solution, excepting a slight residue of iron, &c., from the aluminum, and the portion nesslerised contains its full share of ammonia.

To determine how much aluminum must be dissolved to completely reduce the nitrates, the following experiments were made. The reductions were made in 50 c.c. Nessler tubes, on account of the convenience with which large numbers of tubes can be handled in racks, and the ease with which they are cleaned. (See Table below).

The amount of nitrite present at any point is comparatively small, and disappears promptly when the nitrate is all reduced, thus marking the end of the reaction. If we assume that the first centigram. of aluminum in dissolving reduces 20 per cent of the nitrate, and each additional centigram., 20 per cent of that remaining unreduced, we obtain the figures given in the last column. These agree fairly well with the observed reduction. The proportion of nitrate reduced by insufficient amounts of aluminum is almost exactly the same, whether the standard contains 1 or 10 parts nitrogen as nitrate in 100,000. With more dilute solutions, the proportion was nearly the same, but with stronger solutions the ratio is lower, although the absolute amount of nitrate reduced increases.

With higher temperatures, the solution of the aluminum is much more rapid and a smaller portion of the hydrogen is effective. At 30°, each centigram. of aluminum in dissolving reduces only about 10 per cent of the unreduced nitrate, and so twice as much must be used to obtain a given reduction as is required at 20°. With temperatures lower than 20° the action is very slow, and a long time is required for enough aluminum to be dissolved.

If a large excess of caustic soda is used, the action is also very rapid, and the hydrogen is less effective, but the difference is not so marked as when the action is hurried by increased temperature.

The time required for the action depends upon the surface of the aluminum; the form of the metal has no other influence on the reduction. The same ultimate result is obtained with equal weights of aluminum, other conditions being the same, whatever its shape. With tin foil, the reaction is complete in a few hours, while with thick wire days may be required. When the tubes are allowed to stand over night at room temperature, foil 0.005 inch thick is thin enough, and gives less trouble by floating than thinner foil.

* Jour. Chem. Soc., 1890, 811.

Potassium nitrate solution.				Aluminum.	Caustic soda.	Nitrate	Nitrite.	Nitrogen	Calculated
				Grm.	40 per cent solution.	unreduced.	Per cent.	as ammonia.	reduction.
					C.c.	Per cent.	Per cent.	Per cent.	Per cent.
1 part N in 1000,000	..	..	..	0.01	1	82	2.5	15.5	20
	..	..	..	0.02	1	51.5	2.5	36	36
	..	..	..	0.04	1	35.5	2.5	62	59
	..	..	..	0.10	1	8	3.0	89	89
	..	..	..	0.20	1	0	0.5	99.5	99
	..	..	..	0.40	1	0	0.0	100	99.99
10 parts N	..	..	..	0.01	1	80	1.8	18	20
	..	..	..	0.02	1	63	3.0	24	36
	..	..	..	0.04	1	39.5	3.5	57	59
	..	..	..	0.10	1	15	2.0	83	89
	..	..	..	0.20	1	1	1.0	98	99
	..	..	..	0.40	1	0	0.0	100	99.99
0.1 part N	..	..	..	0.02	1	—	—	32	—
100 parts N	..	..	..	0.02	1	—	—	5	—

At one time we used a cheap caustic soda, containing zinc, because it was entirely free from nitrogen. It dissolved the aluminum freely, but for some unknown reason, the hydrogen evolved was less effective than that from other samples of caustic soda and potash. We thought this might be due to the zinc, but when zinc was added to pure caustic soda no corresponding effect was produced. The use of the soda was discontinued; but no explanation of its action has been found. The presence of sodium carbonate, even in large quantity, does not affect the reduction in any way.

With a majority of waters, the aluminum dissolves much more slowly than in distilled water, or in solutions of potassium nitrate in distilled water. Whatever the cause of this phenomenon, its effect is to make the hydrogen even more effective than with potassium nitrate solutions, as is shown by the following results with a ground water in which the aluminum dissolved very slowly:—

With 0.02 grm. Al.	0.45 part nitrogen reduced.
" 0.10 "	1.03 "
" 0.40 "	1.03 "

The proportion reduced by insufficient aluminum is considerably greater than with potassium nitrate solutions in which the aluminum dissolves more rapidly. Care must be taken in such cases that enough aluminum dissolves. Conditions which are best adapted to the reduction of potassium nitrate often fail completely with waters, because in the time which suffices for the complete reduction of the standard, the reduction of waters with slow action is far from complete. As with the phenolsulphonic acid process, the fact of good results with standards is insufficient evidence of good results with waters.

The absence of nitrites, as shown by the sulphanilic acid and naphthylamine test, is the best evidence that reduction is complete. As long as a decided red is given by these reagents, we may be sure that reduction is incomplete, but when only a slight reaction or no reaction is given, reduction is complete, and no higher results can be obtained by dissolving more aluminum. To obtain this result with waters, in a moderate length of time, it is necessary to use twice as much caustic soda as is required by potassium nitrate standards.

To make the determinations of nitrates in waters, we proceed as follows:—A 50 c.c. Nessler tube is filled to the mark with the water, and about 0.4 grm. aluminum foil 0.005 inch thick added with 2 c.c. of a 40 per cent solution of caustic soda. After standing eighteen to twenty-four hours at room temperature, a portion, 1 to 25 c.c., depending on the amount of nitrate present, is taken out with a pipette, and put in a tube of distilled water free from carbonic acid, which has previously been brought to the same temperature as the ammonia standards. All are nesslerised and compared in the usual way. Blanks and standards are frequently done as a control, and a portion of the waters, after reduction, is tested for nitrites. When nitrites are found in considerable quantity, the determinations are repeated, usually giving a higher result. In calculating the results, the correction for the volume of the caustic soda solution added, and the loss of ammonia with the hydrogen, and the reduction from ammonia to nitrogen, can all be combined in a single factor. When the determination is carried out as above, this factor is 0.88. Thus if 5 c.c. of the reduced water contains 0.05 m.grm. ammonia, 5 c.c. of the original water contained 0.88 of this, or 0.044 m.grm. nitrogen as nitrate. The blank should not exceed 0.005 part nitrogen in 100,000, and can often be neglected. Deduction is made for the ammonia and nitrites, but when the ammonia is a considerable fraction of the total nitrogen, it must be removed by boiling, after adding the caustic soda. In these cases, and also with waters having very low nitrates, especially yellow surface waters, the results obtained in this way are often unsatisfactory, both because the ammonia reading is influenced by the colour of the water, and because

the amount of ammonia obtained is too small for accurate estimation. In such cases, 100 c.c. or more of the water is boiled in a flask with the caustic soda to 50 c.c. The reduction is then made as usual, after which the ammonia is distilled in a current of steam and nesslerised. If the water is concentrated in an evaporating dish, the results are high, owing to absorption of nitrous acid from the gas, but in a flask, the blank is not more than 0.003 part, and is quite constant.

The following determinations of nitrates were made by one of us in solutions prepared by the other:—

Solution taken.	Nitrogen as nitrate taken. Parts in 100,000.	Nitrogen as nitrate found.	
Potassium nitrate.. ..	0.20	0.21	Direct reading.
" " " " "	1.52	1.48	
" " " " "	0.68	0.72	
" " " " "	1.76	1.67	
" " " " "	0.96	0.92	
" " " " "	1.46	1.50	
" " " " "	0.0	0.0	
" " " " "	1.20	1.20	
" " " " "	0.06	0.05	
" " " " "	0.25	0.25	
" " " " "	0.010	0.009	Distilled.
" " " " "	0.044	0.043	
10 parts peptone	0.0	0.013	
10 parts peptone with potassium nitrate	0.027	0.046	
20 parts peptone	0.0	0.028	
20 parts peptone with potassium nitrate	0.030	0.049	
10 parts egg albumen ..	0.0	0.020	
Sewage, albumenoid ammonia, 0.50	—	0.01	
Sewage, albumenoid ammonia, 0.72	—	0.02	

With large amounts of organic matter, the action of the caustic soda and aluminum decomposes a portion of the organic matter with formation of ammonia, as is shown by the experiments with peptone and albumen. As far as our experiments have been carried, this error does not exceed from 2 to 4 per cent of the albumenoid ammonia. With almost all ground waters, and with most surface waters, this error is quite insignificant. It is only in presence of large quantities of decomposing organic matter that the result becomes uncertain. In such cases nitrates are invariably accompanied by nitrites, for if nitrate is added to such a water, a portion, if not the whole, is quickly reduced to nitrite, and in turn, the nitrite is often reduced, after all the nitrate is gone. We are thus able, in many cases, as for example with sewage, to infer the entire absence of nitrates from the low results, and the absence of nitrites. With excessive organic matter and the presence of nitrites, the results obtained can be taken as a maximum limit, and the same less 4 per cent of the albumenoid ammonia, as a probable minimum limit. It should be observed that the nitrate determination in such unusual cases is of minor importance, and that the phenolsulphonic acid process is also quite unreliable under these conditions, the organic matters giving a yellow colour which often corresponds to more nitrate than is shown by the aluminum process.

With potassium nitrate solutions in distilled water, the results are quite satisfactory, being as accurate as the strength of ammonia solutions can be determined at a single trial by direct nesslerisation, and we may believe that our results upon waters, with the above mentioned exceptions, are equally accurate.

Support in Weighing Substances.—H. Schweitzer (*Chemiker Zeitung*) recommends zylonite, a paper made from nitro-cellulose, camphor, and alcohol.

CORRESPONDENCE.

DETECTION OF NITRATES AND CHLORATES.

To the Editor of the Chemical News.

SIR,—The following two new tests for the detection of nitrates in the presence of chlorates, and of nitrates apart from chlorates, will, I opine, be found very simple and effective.

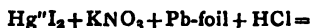
Nitrates in Presence of Chlorates.—Put together in a test-tube $\text{KNO}_3 + \text{KClO}_3 + \text{H}_2\text{SO}_4$ (dilute) + excess of Cu foil. Place test-tube in a beaker holding saturated solution of NaCl, and heat to boiling. The chlorate being least stable is first decomposed, the liberated chlorine attacking the Cu, and a greenish gas given off. At a higher temperature, KNO_3 is decomposed and attacks the Cu, with formation of brown fumes.

Nitrates Apart from Chlorates.—Put into a test-tube $\text{KNO}_3 + \text{Pb}$ foil (shavings) + HCl (strong) and heat; KNO_3 is decomposed and attacks the Pb foil, with formation of $\text{Pb}(\text{NO}_3)_2$, which is again decomposed by the HCl, with formation of PbCl_2 , and will be found as a white precipitate upon cooling.

One great advantage of this test lies in the fact that a nitrate can be detected in the presence of an iodide or bromide, because it is not dependent upon the formation of brown fumes, but upon that of PbCl_2 . Thus—



free Br + PbCl_2 precipitate on cooling. Again,—



free I + PbCl_2 precipitate on cooling.—I am, &c.,

MATTHEW FORBES.

12, Bell Street, Dundee.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. vi., No. 67.

This issue is taken up with reports on the merits of the various inventors to whom the Society has awarded medals or prizes.

No. 68.

This issue contains no chemical matter.

Revue Universelle des Mines et de la Metallurgie.

Series 3, June, 1891. Vol. xiv., No. 3.

Purification of Industrial Waters and Sewage.—

A. and P. Buisine.—The authors prepare ferric sulphate from burnt pyrites by moistening them with concentrated sulphuric acid, so as to form a thick paste. If this is kept for some hours at $100-150^\circ$, with occasional agitation, the pyrites are covered with a whitish layer of ferric sulphate. It produces a more complete purification than does the addition of milk of lime. Water purified with ferric sulphate is perfectly clear, colourless, inodorous, neutral, or slightly acid. On the contrary, the effluent from the lime treatment is alkaline, coloured, retains an offensive odour, and rapidly becomes the seat of putrid fermentation. (Ferric salts have already been used for the treatment of sewage).

A New Method of Separating Iron from Cobalt and Nickel.—G. A. Le Roy.—In order to determine cobalt or nickel electrolytically, it is necessary first to remove any iron which may be present. The author effects this by bringing the metals into sulphuric solution, adding a very small quantity of a non-volatile organic acid, preferably citric. There is then added a large excess of a concentrated solution of ammonium sulphate, rendered strongly ammoniacal. Under these circumstances ferric hydroxide is not precipitated.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 8, August 24, 1891.

This issue does not contain any chemical matter.

Vol. cxliii., No. 10, September 7, 1891.

Direct Synthesis of the Primary Alcohols.—Paul Henry.—Methyl alcohol, H_3COH , is the primordial alcohol. The primary, secondary, or tertiary alcohols are derived from it by the respective substitution of hydrocarbon radicles C_nH_x for one, two, or three atoms of hydrogen. This general idea lacks experimental confirmation as far as the primary alcohols are concerned. The author has supplied this deficiency by the reaction of the organo-zinc compounds upon the simple monoclinic methylic ethers. These, $\text{ClH}_2\text{C}-\text{OCH}_3$ and $\text{ClH}_2\text{C}-\text{OC}_2\text{H}_5$, represent methylic alcohol, in which the hydroxyl group is rendered inactive in consequence of the replacement of the hydrogen by a hydrocarbon group, whilst the reactional aptitude of the chlorine is further heightened by the proximity of the oxygen. The monochloric methyl oxide, $\text{ClH}_2\text{C}-\text{OCH}_3$, and its ethylic analogue react energetically upon the organic zinc compounds. Into these, enclosed in a flask filled with carbon dioxide and strongly refrigerated, chloric ether is let fall drop by drop. There results a thick mass, a mixture of ZnCl_2 and of the ether formed. When the reaction is completed, water is added and the mixture is distilled. The yield of the operation is at least 90 per cent of the theoretical yield.

MISCELLANEOUS.

"A Learned Judge! Mark, Jew, a Learned Judge."—A case was tried at the Belfast Assizes last week in which the plaintiff complained that his clothes had been destroyed and his flesh burned, by reason of the spilling of a corked bottle of aquafortis which had been served to him by the defendant. He had recovered £3 as damages, but was fool enough to appeal against that amount as being insufficient, the result of which was that he got nothing, and had to pay costs. To those who know anything about aquafortis, it may appear strange that any doubt could arise as to the stupidity of putting up that liquid in a corked bottle, but the evidence went to show that it is a custom of the trade to send it out in such way, and the learned judge was certainly not learned on this subject, for he said that he "never heard of aquafortis affecting corks before."—*Medical Press.*

Quantitative Determination of Pyridine Bases in Ammonia.—W. Kinzel (*Pharm. Central Halle*).—The author's method depends on the fact that pyridine and its alkyl derivatives, which in some respects are very similar to ammonia, form very unstable compounds with mercuric chloride, whilst ammonia forms more permanent basic compounds. The pyridine compounds are decomposed on heating and pass over into the distillate. 100 grms. of ammonia are neutralised with sulphuric acid (1:5) with thorough refrigeration (using tincture of litmus as indicator), mixed with 1 drop of soda-lye, made up to 400 c.c., and distilled down to $\frac{2}{3}$ in an hour. The distillate is mixed with 10.0 mercuric chloride in solution again made up to 400 c.c., and again distilled down to $\frac{2}{3}$ in the same time. The solution is again titrated with decinormal hydrochloric acid to a red colour, using dimethyl orange as indicator. As a small quantity of

ammonia always passes over into the distillate, corresponding under the above conditions to 0.8 c.c. of decinormal hydrochloric acid, this quantity must be deducted from the acid consumed. 1 c.c. decinormal acid corresponds to 0.0079 grm. pyridine.

On *a*-Naphthol-Benzene as Indicator.—R. Zoloziecki (*Chemiker Zeitung*).—The author obtains this compound in the following manner:—2 mols. *a*-naphthol and 1 mol. benzotrichloride are diluted in a flask with a suitable quantity of benzol, so as to reduce the violence of the reaction which commences at ordinary temperatures and to yield a much purer product. After standing for 24 hours the reaction is completed by heating to 30–40°, and benzol and the excess of benzotrichloride are driven off by a current of steam. The mass thus obtained is purified by dissolving in dilute soda-lye and fractionated precipitation with hydrochloric acid. This is repeated several times, and finally the colouring-matter is thoroughly washed, and appears as a red-brown powder. Traces of alkalis dissolve *a*-naphthol-benzene with an intense green colour, which is turned to a reddish-yellow by dilute acids. This reaction is occasioned also by carbonic acid, to which this indicator is extremely sensitive. Woollen tissue dyed green with this colouring-matter is turned orange on exposure to the air or on rinsing with spring water. *a*-Naphthol-benzene dissolves in alcohol with a reddish-brown colour. A 1 per cent alcoholic solution is very well suited for volumetric purposes. In its entire behaviour *a*-naphthol-benzene completely resembles phenolphthalein, the only difference being with carbonic acid, since on the addition of an acid to a carbonate the change of colour takes place before the acid salt is formed.

TO CORRESPONDENTS.

J. P. C.—An account of the Kjeldahl process is to be found in Leffmann and Beam's "Examination of Water," p. 31 (Kegan Paul, Trench, Trübner, and Co., Lim.).

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THE CHEMICAL NEWS.

VOL. LXIV., No. 1662.

ON DIDYMIUM FROM DIFFERENT SOURCES.*

By Professor C. M. THOMPSON.

In the *Berichte* of date July 11th, 1887, Krüss and Nilson published observations on the rare earths producing absorption spectra, according to which almost every band observed was found to vary in strength in an independent manner, from which they drew the conclusion that the number of recognised elements must be very largely increased. These observations were continued by Kiesenwetter and Krüss, and the results previously obtained were confirmed.

The interest of these observations is chiefly in the fact that it is very difficult to fit such a number of elements into Mendeleef's system of classification.

It appeared to me important that the purely experimental part of this work should be confirmed or corrected, and as I was in possession of several of the minerals from which the earths may be obtained, I have tried to repeat the observations.

I naturally selected for investigation those minerals from which the most striking results had been obtained, and in order to make my remarks more definite I will confine myself to the consideration of what may be called the didymium fraction. With respect to this fraction, perhaps the most striking results were those obtained by Kiesenwetter and Krüss with the minerals ytrotitanite and gadolinite.

According to them the solution of the earths from ytrotitanite showed only three bands due to didymium, two of them falling together in the broad band in the yellow; the other in the green. Now these are the strongest bands seen with an ordinary didymium solution, and they would of course be seen alone with a very weak solution. I found it impossible to use directly a very strong solution of the crude earths for the examination of the didymium fraction—the bands due to other fractions are so overpowering. The didymium was, therefore, precipitated in the usual way with potassium sulphate. On examining the solution of the nitrates of the earths thus precipitated, I saw, much to my disappointment, what I should describe simply as an ordinary didymium spectrum.

There remains the supposition that the mineral used by me was not the same as that used by Kiesenwetter and Krüss. I can only say that my mineral, like theirs, came from Arendal, and that it agrees in appearance with their published description. There are, however, two differences. The oxides of the earths got by me were of the usual fairly deep yellow colour; they describe their oxides as whitish grey with a tinge of yellow. Secondly, the number of bands not due to didymium, shown by a concentrated solution of my earths, is much greater than that mentioned by them, so that the whole spectrum is quite as complex as that shown by gadolinite earths.

According to Kiesenwetter and Krüss the earths from gadolinite from Hitterö show eight bands due to didymium. Separating the didymium fraction by potassium sulphate as before, I again obtained simply an ordinary spectrum. My gadolinite was from Hitterö.

I have further examined didymium from orthite and from monazite, and have been unable to observe any differences as compared with didymium from cerite which would justify me in concluding that the different bands varied in an independent manner.

I do not wish to deny that there may be slight differences, but they are certainly not such as I was led to expect from Krüss's papers, and they would require either quantitative measurements or direct comparison of the spectra to establish. I hope shortly to make a more careful comparison than I have as yet had time to undertake.

I am of course aware that no amount of negative results are of any value as against well-established positive ones, but I feel that some independent confirmation of Krüss's results is needed, and I can only hope that other chemists will be more fortunate in their material than I have been.

Notwithstanding the above remarks I am inclined to believe that the various bands which used to be ascribed to the one element didymium do vary in an independent manner.

As I pointed out in the *CHEM. NEWS*, vol. lv., p. 227, this conclusion follows from a combination of the results of Crookes and Auer von Welsbach. Only I have not found nature so kind in undertaking the labour of separation as Krüss appears to have done.

University College, Cardiff.

ON AN OPTICAL PROOF OF THE EXISTENCE OF SUSPENDED MATTER IN FLAMES.*

By Sir G. G. STOKES, Bart., F.R.S.
(IN A LETTER TO PROF. TAIT.)

8, Belgrave Crescent,
Edinburgh, June 13, 1891.

DEAR PROF. TAIT,—I write to put on paper an account of the observation I mentioned to you to-night, in case you should think it worth communicating to the Royal Society of Edinburgh.

In the course of last summer I was led, in connection with some questions about lighthouses, to pass a beam of sunlight, condensed by a lens, through the flame of a candle. I noticed that where the cone of rays cut the luminous envelope, there were two patches of light brighter than the general flame, which were evidently due to sunlight scattered by matter in the envelope which was in a state of suspension. The patches corresponded in area to the intersection of the double cone by the envelope, and their thickness was, I may say, insensibly small. Within the envelope, as well as outside, there was none of this scattering. The patches were made more conspicuous by viewing the whole through a cell with an ammoniacal solution of a salt of copper, or through a blue glass coloured by cobalt. In the former case the light from the flame was more weakened than the scattered light, which was richer in rays of high refrangibility; in the latter case the patches were distinguished by a difference of colour, the patches being blue, while the flame (with a suitable thickness of blue glass) was purplish. The light of the patches exhibited the polarisation of light scattered by fine particles—that is to say, when viewed in a direction perpendicular to the incident light, it was polarised in a plane passing through the beam and the line of sight.

When the beam was passed through the blue base of the flame there was no scattered light. A luminous gas flame showed the patches indicating scattered light like the flame of a candle, but less copiously. They were not seen in a Bunsen flame or in the flame of alcohol, but were well seen in the luminous flame of ether. When a glass jar was inverted over burning ether, the blue part, which does not show scattered light, extended higher till, just before the flame went out, the luminous part disappeared altogether. A Bunsen flame, fed with chloride of sodium, did not show the phenomenon, though the flame was fairly luminous.

* Abstract of a paper read before the British Association, Cardiff Meeting, 1891, Section B.

* *Proceedings of the Royal Society of Edinburgh.*

The phenomenon shows very prettily the separation of carbon (associated, it may be, with some hydrogen) in the flame, and at the same time the extreme thinness of the layer which this forms. It shows, too, the mode of separation of the carbon, namely, that it is due to the action of heat on the volatile hydrocarbon or vapour of ether, as the case may be. At the base, where there is a plentiful supply of oxygen, the molecules are burned at once. Higher up the heated products of combustion have time to decompose the combustible vapour before it gets oxygen enough to burn it. In the ether just going out for want of fresh air, the previous decomposition does not take place, probably because the heat arising from the combustion is divided between a large quantity of inert gas (nitrogen and products of combustion) and the combustible vapour, so that the portion which goes to the latter is not sufficient to decompose it prior to combustion.

In the Bunsen flame fed with chloride of sodium, the absence of scattered light tallies with the testimony of the prism, that the sodium is in the state of vapour, though I would not insist on this proof, as it is possible that the test of scattering sunlight is not sufficiently delicate to show the presence of so small a quantity of matter in a solid or liquid state.—Yours sincerely,

G. G. STOKES.

P.S.—I fancy the thinness of the stratum of glowing carbon is due to its being attacked on both sides—on the outside by oxygen, on the inside by carbonic acid, which with the glowing carbon would form carbonic oxide.

PROF. LIPPMANN'S HELIOCHROMY.*

By F. E. IVES.

At the March meeting of this Section I made some comments upon the alleged solution of the problem of photography in natural colours by Prof. Lippmann, of Paris, expressing some doubt as to the possibility of obtaining such alternate zones of "light and darkness" in proximity to the mercury mirror as are called for by Prof. Lippmann's theory, and also as to the possibility of reproducing the compound colours by means of interference lamina. I afterwards communicated my doubt to Prof. Himes, of Dickinson College, and asked for an expression of his opinion. He kindly wrote me a long letter, from which I quote as follows:—

"As far as I have been able to follow Prof. Lippmann I am more hopeful than you perhaps are in the direction of compound colours, and more nearly satisfied with the theoretical explanation, although, of course, at this early stage it must be regarded, of course, only as provisional, and there are many questions that both of us would like to ask, some of which Prof. Lippmann might possibly be able to answer by this time, and others I am just as certain he could not. I will just note hastily the points upon which I have less difficulty and doubt than you seem to have, premising first that you concede the fact that Prof. Lippmann has succeeded in getting a photographic impression of the spectrum in which can be recognised at least the colours in their order,—some say brilliant and perfect,—but I think Prof. Lippmann's account is more moderate and modest. But this is not the greatest feature of Prof. Lippmann's publication. This has been done long ago and by many, and possibly better than he has accomplished it, but he has succeeded in *fixing* it, and that by the ordinary photographic method, and his whole process, withal, is so simple and complete that it invites and encourages experiment with it, which I have great hope will lead to practical results.

"As to his theory we may think what we please. With

me it has this in its favour, that the appearance of all previously obtained heliochromic results by Becquerel and others, whether flowing from systematic investigation or from accident, as in many cases, conforms to that of Prof. Lippmann's results, and can be best described as that of *interference* colours. There are even those who intimate that after all Prof. Lippmann adopted a theory and line of investigation already outlined.

"I have no difficulty in regard to the interference of direct and reflected waves so as to produce so-called stationary waves of definite length and frequency. The ocular demonstration of such waves, usually employed in lectures, by means of a stretched spiral cord or gum tube, attached at one end to a hook, and held at the other end by the hand, on which regularly timed impulses by the hand produce interfering direct and reflected waves, is very satisfactory at this point. The completed analogue in case of sound is to me conclusive of the plausibility of the theory of Prof. Lippmann. Savort, in the early part of the century, and more recently Lord Rayleigh (in 1888), by a series of classical experiments, demonstrated the presence of stationary sound waves, with their spaces of sound and silence, by the interference of direct waves with those reflected from a board, using a sensitive flame to explore the space. A double reflecting surface may be necessary to present interference colours to the eye, as you state, as the rays should both be moving toward the eye; but to produce the stationary luminous undulations, or zones of maximum movement or maximum energy and zones of rest or of minimum movement, of the ether particles, the interference of an incident and reflected ray from one surface will be sufficient condition. These are hardly to be called zones of light and darkness. A ray of light is invisible as such; it produces visible effects, so here the zones of differing energy in the ether particles produce varying effects upon the film in which they are formed—effects which we recognise as photographic.

"These effects are not the production of pigment colours, as up to this time seems to have been the expectation in heliochromy, but they are rather in nature of change of structure, laminated deposits of silver, so to say.

"As to the rendering of compound colours, I have not seen much claimed as accomplished in this direction. There is a well-grounded hope, I believe, but the rendering of the spectrum and the perfect fixing of it are the chief claims of Prof. Lippmann, as I understand it. I would not draw, or allow the theory to draw, the line of the impossible too near to the present achievement to prevent investigation and experiment with compound colours. The whole doctrine of perception of compound colours would not permit us to deny such possibility. Prof. Lippmann has certainly started scientific thought and investigation, as far as heliochromy is concerned, in a new direction, by results that command our admiration and a theory that is not only possible, but a most excellent working hypothesis."

Capt. Abney, who recently visited Prof. Lippmann, also appears to endorse his theories, but does not regard his process as a step in the direction of practical photography in colours. The following report of Captain Abney's remarks upon this subject, at the recent Camera Club Conference, is from the *Photographic News* of April 10th:—

"Photography in natural colours was the next question to which the President turned his hearers' attention. The 'accomplished fact,' as some of the newspapers led their readers to suppose, is as old as photography, for the discovery of photography in colours has been made, according to some people, over and over again. Being in Paris a week ago he had the opportunity of visiting M. Lippmann. He found that gentleman to be a true man of science, with all the modesty of a real investigator. The colour plates about which we have heard so much are due to interference, and not to pigments, and their effect varies according to the angle at which the plate on which they

* A communication to the Chemical Section of the Franklin Institute, April 21, 1891.

appear is held. Capt. Abney then proceeded to describe how these colours are obtained, by use of a mercury trough, as already detailed in our pages. He pointed out that, to obtain the colours, exposure to a bright spectrum was necessary, and that development must be brought about by alkaline carbonates, and the image intensified with silver. Both exposure and development must be exactly correct, or no colours are apparent, and the best results are gained with dry plates prepared with albumen and collodion. He looks upon the results of M. Lippmann's experiments merely as a verification of Newton's law, and not as a discovery of photography in colour. M. Lippmann has certainly succeeded in fixing interference colours, but the process is clearly one of extreme difficulty. It is a misfortune both for M. Lippmann and his predecessor, Dr. Koch, that their experiments should have been dealt with by the ordinary reporters, because these reports have led the general public to expect far more than the experiments in either case justified."

UNIVERSAL MICROSCOPIC EXHIBITION AT ANTWERP.

THE following particulars are obtained from the *Chemiker Zeitung* :—

The "Exposition de Microscopie Générale, de Produits Végétaux et d'Horticulture" has just come to an end. It was projected by Dr. Henri van Heurck, Director of the Antwerp Botanical Garden, a microscopist of reputation. The plan of the promoters allowed of a strange mixture of products. Thus, along with brewed drinks, "schnaps" of all kinds (i.e., inferior liqueurs), were to be found pianos, mineral oils, guano and other manures.

J. D. Möller, of Wedel, in Holstein, exhibited a collection of Diatoms, including not fewer than 4026 distinct forms. Not alone photographs of these species were on view, but the original specimens could be examined under a number of microscopes.

The firm Lumière and Cöller, of Lyon, exhibited coloured transparent figures of microbia, just as they appear to the eye under the microscope.

Along with microscopes there were exhibited stoves for the cultivation of bacteria, apparatus for sterilising, &c.

Among the exhibitors of instruments a prominent place belongs to the establishment of Carl Zeiss, of Jena. Their display included a selection of microscopes, from the simplest to the most complex, combined with appliances for photographic projection, a set showing all the single parts of which a perfect microscope is composed, and a collection illustrating the production of lenses from the crude glass through every stage of grinding.

Watson and Sons, of Holborn, exhibited a large selection of microscopes for various purposes, especially an instrument made according to the indications of Dr. van Heurck, adapted for delicate researches and for photomicrography.

M. Nachet, of Paris, displayed instruments for research, general, scientific, and technical.

Powell and Lealand, of London, exhibit a large microscope, said to be the most perfect as regards its stand. Hartnack, of Potsdam, had microscopes and object-glasses with photo-micrographic fittings. J. Deby, of London, displayed a collection of instruments by various modern makers with manifold appliances for illumination, arrangements for obtaining monochromatic light, as also a rich and interesting collection of preparations. Adnet, and also Wainsegg, of Paris, and Siebert, of Vienna, exhibited a variety of bacteriological apparatus.

It strikes us as remarkable that no spectroscopic apparatus seems to have been exhibited.

The *Chemiker Zeitung* remarks, with perfect justice, that it is impossible for an expert to pronounce on the value of any instrument so long as it can only be seen in a glass case.

ON THE ACTION OF DIFFERENT METALS, METALLIC SALTS, ACIDS, AND OXIDISING AGENTS ON INDIA-RUBBER.*

By WILLIAM THOMSON, F.R.S.Ed., &c., and
FREDERICK LEWIS.

A FEW years ago one of us studied the influence of different oily and greasy matters on india rubber. (*Journal of the Society of Chemical Industry*, 29th December, 1885), and at the meeting of the British Association in Leeds we called attention to the distinctive effect which both metallic copper and all the salts of copper exercised on india-rubber. In the present paper we have carried these experiments further, with a view of obtaining more accurate information as to the effect of copper and its salts, and also that of other metals and their salts, and other agents, on india-rubber.

The method we adopted was to take a fine sheet of india rubber spread on paper and vulcanised by the cold process with a mixture of chloride of sulphur dissolved in bisulphide of carbon. By this arrangement it was easy to tell the effect of different substances on the rubber on breaking the paper between the fingers, the fine sheet of caoutchouc being left free so that it could be stretched, and a fair idea obtained as to whether its elastic properties had been damaged.

Action of Metals on Rubber.

The first series of experiments was made with different metals reduced by means of a file to a fine state of division, the file employed being first thoroughly cleansed, and then washed with ether, to remove any oily or greasy matters from it. Small pieces of 3 inches square were cut from a large piece of the above-mentioned fine sheet pure Para rubber, and thin layers of the filings of the different metals were spread over about 1½ inches square of the centre. These were then placed together in an incubator, kept constantly at a temperature of 140° F. by means of a thermostat, night and day, on glass shelves, and every day the positions of the pieces so treated were altered, so that those in the middle were placed nearer the sides, which we thought might possibly communicate more heat than might be received in the middle. After ten days the rubber on each square was tested in the manner above indicated. This series of experiments was repeated, and the following results were obtained :—

One of the metals had a destructive effect on rubber far beyond any of the others, and that was copper. As compared with copper the following metals had a comparatively slight effect, although they exercised an injurious influence. They are given in the order of the injurious influence they exercised :—

- | | |
|---------------|---------------|
| 1. Platinum. | 3. Aluminium. |
| 2. Palladium. | 4. Lead. |

The following metals were tried, and found to have no effect whatever :—

- | | |
|------------|-----------|
| Magnesium. | Tin. |
| Zinc. | Arsenic. |
| Cadmium. | Antimony. |
| Cobalt. | Bismuth. |
| Nickel. | Silver. |
| Iron. | Gold. |
| Chromium. | |

Action of Metallic Salts on Rubber.

Saturated solutions of a number of metallic salts were made and painted over part of each small sheet of rubber (equivalent to about 1½ inches square), allowed to dry,

* From the fourth volume of the fourth series of *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*. Session 1890-91.

and put into the incubator as above described. Along with each series several untreated small sheets of the same rubber were exposed for comparison, because, after some weeks, the pure rubber will itself become oxidised and lose its elasticity. Some insoluble or difficultly soluble compounds were also employed. These were mixed into thin pastes with water and painted on to the rubber sheets. The following substances entirely destroyed the rubber :—

Copper sulphate.	Silver nitrate.
" chloride.	Strontium chlorate.
" nitrate.	Vanadium chloride.
" ferrocyanide.	Red oxide of manganese.
" oxide.	Black "
" sulphide.	Bismuth chloride.
Arsenic iodide.	

The following substances *considerably damaged* the elasticity of the rubber, but did not entirely destroy it :—

Ferrous nitrate.	Uranium nitrate.
Sodium nitrite.	Ammonium vanadate.

The following substances *only slightly damaged* the elasticity of the rubber :—

Lead chromate.	Tin peroxide.
Ferrous sulphate.	" perchloride.
Zinc acetate.	Chromic acid.
" chloride.	Lead borate.

The following substances were found to have no action whatever on india-rubber :—

Ammonium sulphate.	Aluminium chlorate.
" chloride.	Zinc chromate.
" carbonate.	" nitrate.
Potassium chromate.	" oxide.
" bichromate.	" sulphate.
" cyanide.	Ferric chloride.
" acetate.	" acetate.
" carbonate.	Manganese chloride.
" chlorate.	Cobalt chloride.
" iodide.	Nickel chloride.
" nitrate.	" nitrate.
" sulphate.	Thallium chloride.
Sodium sulphate.	Mercury bichloride.
" sulphite.	" iodide.
" chloride.	Arsenious acid.
" carbonate.	Arsenic acid.
Lithium carbonate.	Bismuth nitrate.
" chloride.	" oxide.
" salicylate.	Cadmium bromide.
Rubidium chloride.	" chloride.
Barium nitrate.	" iodide.
" chloride.	" nitrate.
Magnesia.	" sulphate.
Magnesium sulphate.	Lead chloride.
" chloride.	" oxalate.
Calcium carbonate.	Tin protochloride.
" chloride.	" protoxide.
Strontium chloride.	Palladium chloride.
" acetate.	Gold chloride.
Aluminium sulphate.	

Effects of Minute Quantities of Copper Salts on India-rubber.

We next directed our attention to the influence of minute quantities of the salts of copper on india-rubber. We took small square sheets of the fine sheet rubber, adhering to paper, and painted one with a solution containing 10 per cent of sulphate of copper. On weighing the amount applied to the rubber it was found to be equivalent to 3·84 grains of crystallised sulphate of copper per square foot. This solution was then diluted with its own bulk of distilled water and a second sheet painted

with the diluted solution. This second solution was again diluted with its own bulk of water and a third sheet painted with it, and so on. There were thus prepared six pieces, containing the following quantities of copper salt per square foot of thin sheet rubber :—

	Grains of sulphate of copper (CuSO ₄ ·5H ₂ O).	Equal to grains of copper oxide (CuO).
Sheet (a)	 3·840	1·218
(b)	 1·920	0·609
(c)	 0·960	0·305
(d)	 0·480	0·153
(e)	 0·240	0·076
(f)	 0·120	0·038
(g)	 without copper.	

All these pieces were placed in the incubator at 140° F. for nine days, when it was found that the sample (f) which contained the smallest quantity of copper had entirely lost its elasticity and become quite rotten, whilst the piece (g) which contained no copper was perfectly sound; on examining the others they were all found to have entirely lost their elasticity, and to be hardened exactly in proportion to the quantity of copper salt placed upon their surfaces, (a) being the hardest. It is, therefore, evident that an extremely small quantity of a copper salt has a highly injurious influence on rubber with which it comes into intimate contact. In speaking on this subject to Mr. Thomas Rowley, of Manchester, he informed one of us that when he was an india-rubber manufacturer he had proofed large quantities of cloth with rubber, and had a book in which he kept samples of all he produced, many of which were now fifteen years old. It struck us that it would be interesting to find whether any of the cloths which had been so proofed, and which had remained good for so long, contained copper, and Mr. Rowley very kindly placed his pattern books at our disposal. These patterns were arranged in numbers, describing the nature of the cloth and kind of proof, &c., and dates. We selected seven samples, all of which, except one, had been steam vulcanised, i.e., sulphur had been mixed with the rubber composition before proofing, and the combination between the two brought about by heating with steam afterwards. These patterns were perfectly sound, although about sixteen years old.

We also selected one pattern of a brown cloth, in which the rubber proofing was decomposed and hardened, and which broke on the cloth being folded or bent. Table A is the list of the samples taken.

All these samples were steam vulcanised, except the one marked 7th May, 1875, which was cold vulcanised with chloride of sulphur dissolved in bisulphide of carbon.

We carefully tested the whole of these for copper, and found that all those which were quite sound were perfectly free from it, whilst the sample which had become hard contained a trace of that metal. It appeared, therefore, that this trace was sufficient to bring about the complete destruction of the rubber after a number of years.

It may be well to give, as follow, the results of a series of experiments and analyses of some cloths, the rubber proofing on which was found to be destroyed within a few weeks or months after they were proofed. We pasted together, end to end, 19 samples of cloth, taken promiscuously, in one long line, and had the whole of them cut along the line into five equal parts. Each line of samples was then covered with a continuous sheet of different india-rubber mixtures, and one with pure Para rubber. Strips of each series were cut along the whole line, and then were looped and fixed so as to hang from stretched threads in the incubator, kept constantly at a temperature of 150° F. They were examined from time to time, but, finally, after twenty-five days, they were removed, and their condition noted; and, simultaneously, the analyses of unproofed pieces of the same cloths were made to find whether they contained copper, and the quantity of copper was esti-

TABLE A.

Private numbers.	Date	Description.	Results of analysis.	Condition in Jan., 1891
No. 110.	19 Nov., 1874.	Black alpaca.	Copper absent.	Good.
" 222.	18 Jan., 1875.	" "	" "	"
" 252.	22 Jan., 1875.	" Paramatta.	" "	"
" 411.	2 April, 1875.	Blue-black Paramatta.	" "	"
" —	7 May, 1875.	Black fine sheeting (cold vulcanised).	" "	"
" 982.	28 Aug., 1875.	Brown fine sheeting.	" "	"
" 1150.	24 Sept., 1875.	Drab stout twill (black proofing).	" "	"
" 638.	25 June, 1875.	Brown cambric (black proofing).	" Trace."	Quite decomposed and hard.

TABLE B.

Description of cloth.	Per cent.		Appearance of rubber or rubber composition after being heated in the incubator at 150° F. for twenty-five days, in each of the five series.
	Oily and greasy matters.	Copper CuO.	
1. White and black star check.. ..	0.260	Absent.	Good condition.
2. Dark brown ring check.. ..	0.384	Present, but copper not estimated.	Bad, and quite destroyed.
3. Light " " " " " " " " " "	0.499	" " " "	" " " "
4. Dark brown check.. ..	0.128	Trace.	Damaged, but not quite hard.
5. " " broken check.. ..	0.516	Present.	Hard and quite destroyed.
6. Gold check.. ..	0.548	Absent.	Good.
7. Blue pin head check.. ..	0.648	Present.	Hard and quite destroyed.
8. Ruby hair line.. ..	0.301	Absent.	Good.
9. Drab fine sheeting.. ..	0.264	"	"
10. Black and white small check sheeting.. ..	0.206	"	"
11. Black and white large check sheeting.. ..	0.445	"	"
12. Slate sheeting.. ..	0.181	"	"
13. Blue check sheeting.. ..	0.388	Trace.	Damaged, but not quite hard.
14. Crimson sheeting.. ..	0.471	Not tested.	Good.
15. Black fine twill.. ..	1.500	0.332	Very much damaged, rubber quite hard
16. Black broad.. ..	1.252	Present	" " "
17. Black sheeting.. ..	1.552	0.150	" " "
18. " " " " " " " " " "	2.805	Present.	" " "
19. Black plain muslin.. ..	2.360	0.0157	Slightly damaged.

mated in some of them; the quantities of oily or greasy matters present were also estimated. Table B gives the results of the observations and analyses, and shows that the rubber remained good in all the samples of cloth which were free from copper, whilst it was more or less seriously damaged in all the samples which contained copper, and, still further, the damage sustained was, as nearly as could be observed, in direct proportion to the quantity of copper present.

The following pieces of cloth were analysed by one of us, because the rubber proofing had perished within a few weeks or months after being applied to them. Besides being analysed, a piece of each was taken, and one-third of it cut off and put aside. The oily and greasy matters were then removed from the other two-thirds by washing with ether; the part so washed was next divided into two equal parts, one put aside and the other boiled with 1 per cent hydrochloric acid solution, and washed till all the copper was removed and dried. These three pieces were then joined together, end to end, in a line, and attached to another black cloth similarly divided into three parts, one being left in its original condition, one having all the oily and greasy matters removed, and the third having both oily and greasy matters and copper removed; these were again joined in a line to a piece of grey cloth in its original condition, and to a piece of the same from which the oily and greasy matters were removed. It was, of course, unnecessary to use a third piece of this cloth, as it was free from any trace of copper. The eight pieces thus arranged in one line were divided along the line into two parts; one was covered with a continuous sheet of pure Para india-rubber, the other piece was covered with a rubber composition. Both were vulcanised by the cold process, and afterwards arranged in loops, and hung in an incubator at 140° F. for eight days. After that time

the rubber on both pieces of grey cloth and the two pieces of black cloth, from which both grease and copper had been removed (in both series), was found to be perfectly sound, whilst the rubber on the two black cloths in their original condition, and on the two from which the oily and greasy matters had been removed, but in which the copper remained, were completely destroyed, the effect of the oil and grease in contact with the copper. (Some of the copper contained in cloth is usually found in solution in the oily or greasy matters also present). The effect is to reduce the rubber to the condition of a soft sticky substance, resembling grease in consistency, and to this condition the proofing is soon brought when the oily matter present in copper-mordanted cloths exists in considerable quantity. The mixture thus produced is often absorbed into the fibre of the cloth, leaving it in a somewhat limp and sticky condition; when, however, the oily and greasy matters are removed, the rubber simply becomes hard. It is curious, therefore, to find that the

	Per cent.	
	Oily and Greasy Matter.	Copper Oxide (CuO).
Black Cloth ("I")	3.38	0.29
*Decomposed Proofed Cloth said to be same as above after proofing ("E") ..	—	0.12
Black Cloth ("M")	3.14	1.30
*Decomposed Proofed Cloth, said to be same as above after proofing ("C") ..	—	0.33

* These pieces were prepared by the same manufacturer, and said by the proofer to be from the same lots respectively as the unproofed cloths marked "I" and "M."

presence of copper, even when oily and greasy matters are absent, is almost as destructive to the rubber, on rubber proofed cloth, as when they are also present. The preceding table gives the proportions of oily and greasy matters present in the two samples of dyed cloth above-mentioned, and also the percentages of copper contained in them, and also the proportion of copper contained in two cloths, marked "E" and "C," which had been proofed, and become hard within a few weeks or months. Within the last few years a bright bluish black has been produced by means of copper salt with logwood, or more commonly by dyeing, first with logwood, using iron salts as a mordant, and finishing the dyeing with the use of a copper salt as a mordant; and it will be found that if cloth so dyed be proofed, the rubber will rapidly perish. It is remarkable that cloths proofed with a mixture of india-rubber containing a large quantity of "india-rubber substitute" (vulcanised oil) are not so easily affected by copper salts as those proofed with pure india-rubber. A curious piece of evidence as to the action of copper on rubber came into the hands of one of us, after proofing the above-mentioned pieces, which had been divided into three parts as above described, and obtaining the results just given. A chemist placed in our hands two pieces of the same black dyed cloth, which, he said, were produced by the same manufacturer, and proofed by two different proofers. He said he had heated part of them to 150° F. for a week, and they had not become injured in any way. Both pieces were analysed, and found to contain—

		Percentage of Copper Oxide.
India-rubber waterproofed cloth ..	(a)	0.190
" " " " " " " " " " " "	(b)	0.108
Cloth "before proofing" ..	(c)	0.370
The oily and greasy matter in cloth before proofing amounted to ..		4.200 %

Wishing rapidly to arrive at a conclusion as to the influence of the copper oxide on the rubber, we heated pieces of both at the temperature of boiling water for twelve hours, along with two other pieces which were two and five years old respectively, and at the end of that time the rubber on the cloth containing copper was in the one damaged and in the other destroyed, whilst that on the two free from copper was quite sound.

We might give still another instance in which some black, brown, and white-check proofed cloth, the rubber on which had become oxidised and hard, was analysed by one of us, and found to contain 0.24 per cent of copper oxide: he afterwards obtained some unproofed cloth of the same kind, which he divided into three parts; one he left in its original condition, from one he extracted oily and greasy matters, and from the third he removed the copper as well as the oily and greasy matters; the three were joined together and covered with a continuous sheet of pure Para india-rubber by one proofer, and a second portion of these three pieces, joined end to end, was covered with a continuous sheet of ordinary rubber composition, containing lampblack, zinc oxide, and other mineral compounds, by another proofer. On heating these for fourteen days in the incubator, at a temperature of 150° F., the pure rubber and the rubber composition on the cloth from which the oily and greasy matters and copper were removed remained quite sound, whilst the proofed cloth, in its original condition, and in that from which the oily and greasy matters had been removed (leaving the copper), both the rubber and rubber composition had become quite hard.

The following gives the proportion of oily and greasy matters, and of copper contained in the unproofed cloth:—

	Per cent.	
	Oily and Greasy Matters.	Copper Oxide (CuO).
Unproofed black, brown, and white-check cloth ..	0.68	0.076

We think no stronger proof is necessary to show the enormous influence which a very small quantity of copper contained in cloth has upon india-rubber or rubber composition with which it may be covered or proofed.

We were under the impression that the action of copper on rubber had never been noticed by practical men employing rubber which requires sometimes to come into contact with copper. Speaking, however, to an electrical engineer and copper wire manufacturer who covers his wires with india-rubber, he informed one of us that the injurious action of copper on rubber was well recognised in his trade, and that to prevent this injurious action it was necessary to have the copper wire tinned, which was always done. We mentioned the matter to other electrical engineers, and found that all were quite cognisant of the injurious effects of copper wire on india-rubber. We found that copper filings also exert a highly injurious influence on thin sheets of gutta-percha when placed together in a warm place.

In looking at the effects of various chemical substances on india-rubber, it will be observed that the oxides of manganese have also a destructive effect on rubber, although not to such an extent as the copper salts; still it is important to india-rubber waterproof manufacturers, who are anxious to remove all possible causes of ultimate damage to their rubber or rubber composition covered cloths, to observe that the lamp black, ivory black, or other similar black, is free from the oxides of manganese, for one of us has found that in samples of such black compounds the heavy qualities sometimes contain a considerable proportion of these compounds.

The very curious nature of india-rubber is further shown by studying the tables of the actions of different chemical compounds on it. Some chemists have condemned cloths containing oxides of chromium for rubber proofing purposes, and they would regard the presence of even a trace of chromate or bichromate of potash as fatal, and the presence of free chromic acid in cloth would be regarded by them as an agent likely almost immediately to oxidise and destroy the rubber. Our experiments have shown that these bodies have little or no injurious effect on rubber, even when employed in large quantities and in concentrated solutions. It therefore leaves the logwood chrome blacks as available for use in the dyeing of cloths intended for rubber proofing. We observed a remarkable property of the iodide of arsenic, which we found might be used as a reagent to determine whether rubber sheet had been cold or steam vulcanised. When a solution of this substance is put upon india-rubber, vulcanised by the cold process, which consists in the application to the rubber of a mixture of chloride of sulphur and bisulphide of carbon, the chlorine from the chloride of sulphur, which remains in combination with the rubber, liberates the iodine from the iodide of arsenic solution, producing a dark stain, whilst no such effect is produced by unvulcanised india-rubber, or by rubber which has been steam vulcanised.

Action of Acids on India-rubber.

We have heard it asserted, from time to time, that a trace of sulphuric acid contained in india-rubber would soon determine its decay and decomposition. With a view to testing this point we took different acids, which were all brought to the same strength, viz., that 100 parts of the different acid solutions neutralised 100 parts of a 10 per cent solution of anhydrous sodium carbonate. These acids were placed in stoppered bottles, two bottles being half-filled with each acid solution, into each of which was immersed a thin sheet of rubber on paper as above described, about 2½ inches square; one of each was placed in the incubator and kept at 140° F. for a month, and the other kept during that time in the cold, the rubber in each being tested from time to time to ascertain whether the acids had any effect upon the sheets. The following acids were employed:—

Hydrochloric acid.	
Sulphuric	"
Nitric	"
Chromic	"
Citric	"
Tartaric	"

In the first four the paper in the heated samples to which the fine sheet rubber was adhering was soon reduced to a pulp, leaving the sheet of rubber intact. After a few hours it was evident that the rubber in the nitric acid placed in the incubator had been seriously damaged, and after a few days it was so acted upon that its elasticity was destroyed, and after a month the whole of the rubber was reduced to a pulp, whilst at the end of the month the sheets of rubber in all the other acids remained as strong and elastic as they were on being first immersed. The sulphuric acid solution which had been heated in the incubator had darkened the colour of the rubber, but, so far as we could judge by stretching, it seemed to be stronger and more elastic than the original rubber. With a view to finding the effect of a minute quantity of sulphuric acid on india-rubber, we soaked a piece of thin sheet rubber in solutions containing 1-10th, 1, 2, and 5 per cent of sulphuric acid respectively, until the solution had thoroughly penetrated the sheet, which then appeared white. This was allowed to dry, and heated for some days to a temperature of 140° F., but the small quantity of acid exerted no injurious effect on the rubber. When, however, the rubber was taken from the strongest sulphuric acid solution containing 10 per cent of acid, dried and heated to 212° F. in a similar manner, it was soon destroyed. The sheets left in the cold for a month were likewise all sound except that placed in nitric acid, which was rendered quite friable, the elasticity having entirely gone.

Effects of Over Mastication on the life of India-rubber

It has been so often asserted by india-rubber manufacturers that over mastication seriously damages india-rubber and leads to its rapid decay afterwards, that it seems extremely heterodox to say anything to the contrary. Still the results which we have obtained lead us to this opinion. In preparing rubber for spreading on cloth in the manufacture of waterproof fabrics, it is first passed between heavy rollers with a stream of waver pouring over it, to remove stones or dirt which might be associated with it; it is then dried thoroughly and masticated between large heavy smooth rollers for a few minutes, these being gradually screwed closer and closer together during the operation. This softens the rubber, and enables it afterwards to be brought into a uniform solution when mixed with the naphtha, and the longer it is masticated the less naphtha is afterwards required to bring it to the proper uniform consistency for spreading. It is highly improbable that over mastication would ever be done in practice, because the workman has to collect the rubber under the rollers and pass it repeatedly through them till it attains the necessary degree of softness, so that as it becomes over masticated it becomes soft and sticky, a point to which any experienced workman would not bring it. About four minutes is required for proper mastication, but one of us prepared some rubbers which were masticated for 15 and 21½ minutes respectively, and after spreading these on cloth we had a piece of the same cloth covered with properly masticated rubber (masticated during four minutes). All these were then placed in an incubator at 150° F. for a fortnight, but the sample of over masticated rubber did not show any sign of decay after that time, and to-day—six months after the experiment was made—the one appears quite as good as the other. The over masticated rubber had, when first produced, a slightly greater "tacky" feel than the properly masticated rubber, and this tackiness appeared not to have become greater or less after the lapse of six months.

Peroxide of Hydrogen.

The curious effect, or rather absence of effect, which chromic acid had upon india-rubber led us to make an experiment to find whether peroxide of hydrogen would oxidise and destroy it. We placed sheets of rubber both in alkaline and in acid solutions of that reagent for one month, and found that after that time the elasticity and strength of the sheets so treated remained unimpaired,—a result which appears quite as surprising as the chromic acid result. Some years ago one of us found that ozone exercised a most injurious influence on india-rubber, especially when it was left in a stretched condition, and it might naturally be expected that peroxide of hydrogen would have exercised an equally injurious influence on it.

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.

(Continued from p. 160).

XLVI.—Phosphorus.

1. MAGNESIUM salts are especially adapted for the detection of phosphorus in compounds which have been opened up by fusion with alkalis. Alongside a drop of the solution in question there is placed a second drop containing magnesium sulphate and ammonium chloride, the port-object is heated, and the two drops are made to coalesce by the addition of a drop of water, or of ammonia if no free alkali is present. Compare Magnesium 1. The limit of the reaction is at 0.000008 m.grm. P.

2. Ammonium molybdate is applicable in the examination of acid solutions in which ammonia would throw down insoluble phosphates. The precipitation ensues at the common temperature. It is accelerated by heat, but it must be remembered that arsenic molybdate and silico-molybdate may be deposited on the application of heat. Ammonium phospho-molybdate agrees with the analogous potassium salt. Compare Potassium 2. On thin slips of minerals containing apatite or phosphorite, a mixture of ammonium molybdate with rather strong nitric acid (1.3 specific gravity) applied in a thin layer and in the cold, gives a reaction which is very well localised. The limit of the reaction of ammonium molybdate with phosphoric acid has its limit at 0.000015 m.grm. P.

XLVII.—Nitrogen.

1. Nitrites can be recognised by means of potassium iodide and starch. Dilute sulphuric acid is applied, a few starch granules are suspended in the liquid, and lastly a little potassium iodide is introduced. Compare Iodine 5. Nitrates are reduced to nitrites by boiling with zinc or magnesium powder. More effective is fusion at dull redness on a nickel wire coated with lead. The limit of the reaction is at 0.00025 m.grm. HNO₃. If iron or manganese is present the conversion into ammonia is to be preferred.

2. Ammonia can be recognised without previous distillation as ammonium-magnesium phosphate. The solution in question is mixed with a little magnesium phosphate, and there is placed near it a drop of water in which sodium phosphate and bicarbonate have been dissolved. A gentle heat is applied and the two drops are caused to flow together. If calcium is present, magnesium chloride and soda-lye must be used, but it is difficult to avoid flocks of magnesium hydroxide. The limit of the reaction is about 0.00005 m.grm. NH₃.

Ammonia which has been isolated by heating with soda-lye, and receiving the vapour in sulphuric acid, is best recognised by means of platinum chloride in the same manner as potassium. Compare Potassium 1. The limit is here at 0.0001 m.grm. NH₃.

* Zeit. Anal. Chemie.

In order to detect nitrates in this manner the specimen is distilled with soda-lye and zinc-powder, and the same degree of sensitiveness is reached as in reduction to nitrites.

3. Most cyanides can be decomposed by caustic potassa. In this case it is sufficient to heat the strongly alkaline liquid with a small admixture of ferrous and ferric chloride, and then without much stirring to add dilute hydrochloric acid. As the iron hydroxide dissolves, flocks of Prussian blue appear. Mercuric cyanide requires to be reduced on bright iron with the addition of potassalye. The limit of the above reaction is at 0.00007 m.grm. CN.

XLVIII.—Sulphur.

1. Calcium salts give in neutral and acid solutions of sulphates a crystalline precipitate of $\text{CaSO}_4 + 2\text{H}_2\text{O}$. Compare Calcium 1. Sulphides must be prepared by fusion with saltpetre and soda, and insoluble sulphates by fusion with soda; the melt must be extracted with water, and the solution acidulated with acetic acid. The limit of the immediate reaction lies at the 400 fold dilution of the sodium sulphate. Beyond that limit the reaction may be masked by the presence of a large quantity of alkaline salts. As regards other disturbing influences, compare Calcium 1. Limit of the reaction 0.0002 m.grm. S.

2. Cæsium chloride, along with aluminium chloride, occasions in solutions of sulphates the formation of colourless octahedra of cæsium-alum. Compare Aluminium 1. This reaction is less simple than the former, but it is less readily masked by alkaline salts, and it is not interfered with by salts of iron. Its limit lies at 0.00012 m.grm. S.

3. Lead salts, on account of the minuteness of the crystals of lead sulphate, are used only for very dilute solutions of sulphates, or for such as are very strongly contaminated by other salts. The limit of immediate action is at a 40,000 fold dilution of sodium sulphate. Compare Lead 3. The limit of the reaction is at 0.000006 m.grm. S.

XLIX.—Selenium.

1. Magnesium, or in its place zinc, reduced slightly acidulated solutions of selenium dioxide. The selenium is deposited as a coating upon the magnesium. If, after a few minutes, the magnesium is dissolved by the addition of hydrochloric acid, there remain, if more than 0.05 per cent of selenium was present, complete impressions of the metallic fragments which are translucent with a deep red colour. From quantities of selenium below 0.02 per cent we obtain red flakes. The limit of this reaction is at 0.0001 m.grm. Se. The limit of the reduction by means of sulphur dioxide is at 0.02 m.grm. Se, according to Streng.

2. Potassium iodide throws down from solutions of selenium dioxide scarlet, pulverulent, selenium tetraiodide. In solutions of seleniates the precipitation occurs only after heating with hydrochloric acid. Selenium iodide sublimes more readily than selenium; the sublimate does not differ in appearance from one of selenium. In an excess of potassium iodide there are formed orange or blood-red ribs and tables which may be mistaken for antimony iodide. By water they are decomposed, with liberation of amorphous iodide. The limit of the reaction is at 0.001 m.grm. Se.

(To be continued.)

The Phylloxera.—According to the *Chemiker Zeitung*, Prof. Perroncito, of Turin, has discovered a very efficient remedy for the Phylloxera. It is a liquid harmless to the vines and to the workmen, but rapidly fatal to the insect. Experiments made upon more than 200 vines in the Province of Porto Maurizio were very successful, whilst the expense of the treatment did not exceed 5 centimes per vine.

ON A COMBINATION OF WET AND DRY METHODS IN CHEMICAL ANALYSIS.*

PART I.

By W. E. ADENEY, F.I.C., Assoc.R.C.Sc.I., Curator, Royal University of Ireland; and T. A. SHEGOG, A.I.C., Assoc.R.C.Sc.I., Assiat. Chemist, Royal College of Science, Dublin.

PLATTNER, in his work on the blowpipe,† states that, when the oxides of the metals are fused on charcoal with borax and sodium carbonate in the R.F., some are reducible and some non-reducible to the metallic state; and he has suggested a general scheme for the analysis of minerals based upon the possibility of separating the reducible from the non-reducible oxides when so treated. Plattner's scheme involves the employment of wet as well as dry methods of analysis. About 1 decigram. of the substance is mixed with about 1 part of fused borax and 1 of sodium carbonate; the whole is wrapped in a little cylinder of soda-paper, and fused before the blowpipe in a hole on charcoal. As the quantity of reducible oxides is usually too small to obtain them in a single bead, about 1 decigram. of metallic silver or gold should be added, in the form of a button, to take up the reduced metal as it is formed. In this way it is stated that a preliminary separation of the reducible from the non-reducible oxides may be effected. The reducible oxides are said to be these of the following metals:—arsenic, antimony, silver, mercury, copper, bismuth, thallium, lead, tin, zinc, indium, cadmium, and nickel. The volatile metals escape, either partially or wholly, during the fusion. The non-reducible oxides are those of the alkaline earths and of chromium, aluminium, iron, manganese, cobalt (in the absence of arsenic acid, and when not present in too large quantity), molybdenum, tungsten, and titanium.

The importance of Plattner's scheme, if it be generally applicable, cannot be exaggerated, for it permits the adoption of one general method of procedure for the qualitative analysis of all minerals, and avoids many of the difficulties attendant upon purely wet methods, such, for example, as the solution of substances, &c.; and, owing to its comparative simplicity, it is quite possible to teach the method to students in geology and engineering, who ordinarily cannot afford to devote sufficient time to master purely wet methods of mineral analysis.

Some time ago one of us framed a complete scheme for the analysis of minerals, based upon Plattner's methods. The substance was to be fused with silver chloride, borax, and sodium carbonate on charcoal in the manner described by Plattner. In cooling the metallic end glass beads were to be carefully detached, one from the other, and separately examined by wet methods in the ordinary way.

Complex minerals, such as tin pyrites and smaltine, were analysed, as directed in this scheme by Mr. F. C. Forth—a student in the Faculty of Engineering in the Royal College of Science, with excellent results. The following are the results of his analysis of smaltine:—arsenic, bismuth, copper, nickel, cobalt, iron, aluminium, manganese, calcium, magnesium, sodium, siliceous matter, hydrosulphuric acid, and phosphoric acid.

On comparing these results with those of an analysis by the ordinary wet methods, it was found that potassium only had escaped detection.

When, however, the method was tried with iron and zinc ores, unsatisfactory results were obtained—results which were in some cases not what we had been led to expect from a perusal of Plattner's book—for instance, with the ores mentioned, the glass bead fused fairly easily, but the metallic bead immediately on reduction became quite infusible, and could not be properly separated from the glass.

* From the *Scientific Proceedings of the Royal Dublin Society*.

† English edition of Plattner's "Manual of Analysis by the Blowpipe," edited by J. H. Cookeley, pp. 116, et seq.

Plattner, in describing his process and the results obtainable by it, makes no mention of such action. Egleston, too, in his scheme makes no reference to it.*

On examining Plattner's work carefully, it was seen that no exact experimental evidence was given by him in support of his classification of the metals into "reducible" and "non-reducible," according to their behaviour on fusion with borax and sodium carbonate on charcoal, in the reducing flame.

It became evident to us from these and other preliminary experiments, that Plattner's method was not one by which easily reducible oxides and difficultly reducible oxides could under all conditions be completely separated. The same may be said of Egleston's method.

The results, however, obtained by Mr. Forth in the analysis of smaltine and tin pyrites were, as above stated, so satisfactory as to convince us of the value of the method if carefully worked out. We therefore determined to make an exhaustive series of experiments, in order to ascertain exactly how the various metals behave when their compounds are fused with borax and sodium carbonate on charcoal in the reducing flame in presence of silver.

We were further encouraged to make these experiments by some quantitative estimations of the nickel, cobalt, bismuth, and copper in the smaltine, made by Dr. L. Davoren, who was at that time studying in the laboratory of the Royal College of Science. Dr. Davoren determined these constituents both by the ordinary wet method and by the proposed combination of wet and dry processes. His results were as follows:—

Ordinary Wet Method.		Wet and Dry Processes.	
	Per Cent.		Per Cent.
Nickel ..	7.60		7.31
Cobalt ..	3.73		3.92
Bismuth ..	2.32	I. ..	3.33
		II. ..	3.35
		III. ..	3.33
Copper ..	1.80		2.06

These results led us to hope that the method might (possibly with some modifications) be found capable of employment for quantitative as well as for qualitative analysis.

The questions we wished to settle by our experiments were:—

1. Whether, when fused in the reducing flame on charcoal with borax and sodium carbonate, the metals antimony, tin, lead, arsenic, silver, bismuth, copper, nickel, and zinc could be completely reduced from their combinations with oxygen with the volatile acids, hydrochloric, sulphuric, nitric, and hydrofluoric; and also from their combinations with the non-volatile acids, silicic and phosphoric.

2. Whether, when similarly treated, aluminium, chromium, manganese, cobalt, and iron are wholly non-reducible from their compounds; the cobalt and iron more especially from their combinations with arsenic and phosphoric acids.

3. Whether, when complex substances are similarly treated, the constituent metals thereof respectively behave as in simple compounds, or whether their behaviour is modified in any way.

The subject-matter of the present paper deals mainly with questions Nos. 1 and 2. A considerable amount of

work has also been done bearing upon question No. 3, but it is proposed to deal with this, and with separations by this method, in a further paper by one of us.

Tables are appended giving the results of some of our experiments

(To be continued).

NOTICES OF BOOKS.

Engineering Chemistry: a Practical Treatise for the Use of Analytical Chemists, Engineers, Iron Masters, Iron-Founders, Students, and others. Comprising Methods of Analysis and Valuation of the Principal Materials used in Engineering Work, with numerous Analyses, Examples, and Suggestions. By H. JOSHUA PHILLIPS, F.I.C., F.C.S., Analytical and Consulting Chemist to the Great Eastern Railway, Author of "Fuels, Solid, Liquid, and Gaseous: their Analysis and Valuation." London: Crosby Lockwood and Son. Crown 8vo., pp. 312.

THE chemical properties of many articles used in what is somewhat loosely called "engineering work" are necessary data for determining their value. Hence we need not prove that the author in collecting together a series of well-proved methods for the analysis of such materials has rendered no small service to a numerous body of practical men.

The introductory chapter of the work is occupied with an account of the Reddrop "equivalent system" of reagents—a full account of which will be found in the CHEMICAL NEWS (vol. lxi., pp. 245, 256).

In Part I. Mr. Phillips proceeds to the analysis of metals and alloys, including white-lead. Next follow ores, limestones, boiler incrustations, clays, blast-furnace slags, &c. In Part III. the author embodies the substance of his former valuable work "Fuels, Solid, Liquid, and Gaseous" (Crosby Lockwood and Son, London). Part IV. is concerned with water. All that is said concerning water for steam-purposes, and the determination of its possible mineral constituents, is perfectly to the purpose, and will be found trustworthy.

In a number of analyses of American samples we regret to find that "the constituents have been stated in grains per U.S. gallon of 231 cubic inches, rather than in parts per 100,000, the former being in general use by the mechanical profession as the proper method by which to express the weights of the component parts of water." This method seems to us devoid of any advantage. Chemists, medical men, &c., in Britain state the contents of water (other than H₂O), either in grains per imperial gallon (=70,000 grains) or in grains per 100,000, or in parts per million, or again, as do our Continental colleagues, in grms. per litre. The introduction of an additional scale can merely tend to confusion.

The injurious effects of magnesium chloride in steam waters are clearly pointed out. The examination of water for drinking purposes can scarcely be said to belong to engineering chemistry. For the determination of free and albumenoid ammonia the author uses the well known Wanklyn process. Concerning the microscopic and biological methods for the examination of drinking waters, the author merely remarks that "many of the diseases that human flesh is heir to are propagated through the drinking of water contaminated with microscopic creatures."

We are little edified at finding here a reproduction of the "standards" of the Rivers' Pollution Commissioners. The errors in principle and the inconsistencies in detail of these "recommendations" have been so often and so ably exposed that charity to their authors, no less than to the public, demands their consignment to oblivion.

The section on oils, lubricants, illuminants, and on materials serving for promiscuous purposes, is admirably written and will be found very useful.

* Egleston, in his scheme, confines himself almost exclusively to dry methods. His method of preparing the glass bead is different to that employed by Plattner. He dissolves the substance in a borax bead on platinum wire, and, when saturated, tosses it off into a porcelain dish, and repeats this operation until a number of beads have been obtained. He then treats the beads on charcoal with lead, silver, or gold in the reducing flame; separates the metallic from the glass bead, and examines each separately by dry methods. The only use he makes of the wet way is in the examination of the borax bead for chromium, titanium, molybdenum, niobium, tungsten, and vanadium. The metals which, according to him, may be present in the metallic bead, are nickel, copper, silver, gold, tin, lead, and bismuth (tin, lead, and bismuth being partially volatilised).

In the four remaining parts the author discusses the materials used in grease-making, gas-works products, disinfectants—which seem somewhat out of place—and explosives.

An appendix of useful tables completes the work.

The analytical methods may be pronounced most satisfactory, being as accurate in their character as the dispatch required of engineering or, indeed, of all industrial chemists permits.

The only alterations we can suggest is a re-calculation of the analyses of boiler-waters—pp. 164 and 165—either to the imperial gallon or to 100,000 parts.

The Metallurgy of Silver. A Practical Treatise on the Amalgamation, Roasting, and Lixiviation of Silver Ores, including the Assaying, Melting, and Refining of Silver Bullion. By M. EISSLER. Second Edition, Enlarged, with 150 Illustrations. London: Crosby Lockwood and Son. Crown 8vo., pp. 362.

THE metallurgical writings of M. Eissler are so highly appreciated by competent judges that we are by no means surprised that a second edition of the work before us has become necessary.

Upon the whole the present edition differs so little from its predecessor that what we have already said at its appearance requires no modification. A defect, or rather an inconvenience, for the English reader is that the yields of different ores by the processes described are expressed neither in percentages nor in the weights of precious metal per ton, but in its value as expressed in American money.

The supplementary chapter gives an account of the Boss "one level system and amalgamating pan," of Brunton's ore sampler, of roasting with salt, with the question what furnace to adopt, of the Bowers and the Thompson furnaces, and a very interesting notice of the behaviour of other metals in the amalgamation of silver ores.

M. Eissler does not think that silver ores carrying even a considerable proportion of oxidised copper yield a cupriferous bullion in the Washoe process. The presence of copper amalgam in the mercury is very beneficial in silver extraction. Lead is not a desirable substance in amalgamation. Zinc is usually expelled by roasting prior to amalgamation.

Iron, it appears, is capable of amalgamating with mercury, but under what conditions it is still doubtful. It is "one of the prime motors in furthering the amalgamation of silver." Antimony is generally expelled by roasting, as is also arsenic, which is a "bad metal to get into the pans,"—a very true remark.

Manganese, in roasted ores, is apt to form a thick froth which holds fine particles of mercury in suspension.

article on the skins of infants; or in other cases the certificates may state that a certain food for infants contains everything that is requisite for the healthful nutrition of children, whereas *bona fide* analyses may show that it is deficient or wanting in some of the ingredients essential to infantile alimentation, and the experience of its sole use as a food may be that it is the causative factor of rickets, or of the scorbutic condition, in children.

The sale of such certificates is, in my opinion, degrading to the profession of chemistry, immoral on the part of those from whom they emanate, and misleading to the public; and those who sell such certificates for money are unworthy of the title of professional men. This prostitution of the science of analytical chemistry must be checked if analysts wish their profession to take its place in the estimation of the public as a calling worthy of the name of a learned profession.

Bearing in mind the fact that each Fellow of the Institute of Chemistry signs a declaration to the effect that he will demean himself honourably in the practice of his profession, and to the utmost of his power maintain the dignity and welfare of the Institute, I have for some time been wondering if the Censors of the Institute of Chemistry are an existing body, and, if so, why signs of their existence are not evident to us. Surely part of their duties must be to exercise a controlling power over the professional actions of those Fellows of the Institute who have the bad taste to allow their names to be flaunted before the public in connection with certificates of a puffing description; certificates which too frequently bear the impress, not of the results of analysis, but of statements which, to put it mildly, are frequently exaggerated, and, to put it less mildly, are frequently untruthful.

I am fully aware that many will retort that these things are done by some members of the medical profession. While admitting that such, unfortunately, is the case, yet two wrongs do not make a right, and certainly such things are not done at the present time by members of the higher ranks of the medical profession. As regards the section of the medical profession to which I belong, viz., physicians, the College of Physicians of London exercises, through its Board of Censors, a strict supervision over the Fellows and Members of the College, and, in my opinion, it would be well if a similar strict supervision were exercised by the Censors of the Institute of Chemistry over the Fellows and Associates of the Institute.

As a Fellow of the Institute of Chemistry I sincerely hope that it will soon rise from the level of a mere examining body to that of a body exercising a just, but vigilant, supervision over the actions of its Fellows.—I am, &c.,

ARTHUR P. LUFF, M.D., B.Sc. (Lond.), F.I.C.

47, Weymouth Street, W., Sept. 25, 1891.

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY AND ADVERTISING CERTIFICATES.

To the Editor of the Chemical News.

SIR,—For some time past it has been no uncommon occurrence to those who read the advertising columns of the daily papers, journals, &c., to see advertised copies of certificates of analyses, or certificates without any analysis appended, given by analytical chemists after whose names the letters F.I.C. appear. In some cases these certificates may state that a certain article is incapable of injuriously affecting an infant's tender skin, whereas the experience of physicians may be that it is by no means an uncommon occurrence for eczema, or some other skin disease, to result from the use of such an

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 11, September 14, 1891.

On the Ferment of Wine.—A. Rommier.—The author adduces further experimental evidence that the bouquet of a wine depends on the ferment employed, and that by utilising this fact ordinary vineyards may be made to produce wines equal to the "*grands crus*" of Burgundy. (The question arises whether the ferments of the choicest French, Rhenish, and Hungarian wines may not be communicated to the growths of South Africa and Australia?)

Zeitschrift für Analytische Chemie.
Vol. xxx., Part 2.

Contributions to Micro-Chemical Analysis.—H. Behrens.—(Already inserted).

Conversion of Free Nitric Acid into Ammonia by Nascent Hydrogen.—Dr. Karl Allsch.—This paper requires the accompanying illustrations.

Liquoscope: an Instrument for the Optical Comparison of Transparent Liquids.—Klas Sonden.—This paper cannot be intelligibly reproduced without the four accompanying illustrations.

Densimetric Determination of Phosphorus in Crude Iron.—E. E. Metz.—This memoir also requires an illustration.

Glaser's Method of Determining Ferric Oxide and Alumina in Phosphates.—Dr. von Gruber.—The author defends Glaser's method against the strictures of Dr. Theodor Meyer.

The Aldehyd Reaction of U. Gayon.—H. Borntrager.—Already inserted.

Improved Apparatus for the Determination of Carbonic Acid.—Greiner and Friedrichs.—This paper depends on the accompanying diagram.

Use of Mohr-Westphal's Balance.—A. Gawalowski.—The author points out as a difficulty in the use of the Westphal balance, that the fine platinum wire by which the thermometer-float is suspended easily becomes bent and is difficult to straighten. This can be easily effected by stretching it horizontally whilst being passed through the flame of an ordinary spirit lamp.

Determination of Manganese in Iron and Steel.—L. Blum.—Already inserted.

The Visible and Ultra-Violet Emission-Spectrum of Burning Faintly Luminous Hydrocarbons.—J. M. Eder.—No particulars are given, the reader being referred to the *Denkschriften der Mathematisch Naturwissenschaft. Classe de K. Akademie der Wissen in Wien*, vol. lvii.

A Spectro-Saccharimeter.—P. Glan.—This instrument, which is described at great length, is intended for accurate determinations of the deviation of the plane of polarisation of light, and for rendering such measurement practicable for every colour of the spectrum.

A Crystal Refractometer.—S. Czapski.—The principle of this instrument is the same as that of Pulfrich.

The Application of Lunge's Gas Volumeter to the Determination of Tensions.—Herm. Rey.—Not adapted for abstraction, requiring the appended tables.

Determination of the Specific Gravity of Rare and Costly Substances.—Aug. Eichhorn.—The instrument has the form of a hydrometer. Between the mercury bulb and the empty float a hollow globe is blown on the stem containing the liquid to be weighed. The stopper is inserted in such a manner that no air globules remain within, and the whole is set in a vessel filled with water at 15° or 17.5°. A scale fixed to the instrument gives the direct specific gravity.

A Table of Corrections for the Gas-Balance of Lux.—R. Mehrke.—The table is not given here.

Thermometers and Measurements of Temperature.—H. F. Wiebe.—Mercurial thermometers filled with nitrogen may be used for the determination of temperatures even exceeding 450°, if they have been previously protected by prolonged heating, and if they are so constructed that the pressure exerted by the nitrogen upon the mercury at 450° is about 4.5 atmospheres.

Thermostats and Thermo-regulators.—O. Foerster.—Not adapted for abstraction.

Air-Bath.—A. Adams.—From the *Analyst*.

A Small Trial Filter.—P. Boesneck (*Chemiker Zeitung*).—A simplification of the tube filter described in "Mohr's Manual of the Volumetric Method."

Apparatus for Distilling Mercury in Vacuo.—Dunstan and Dymond.—From the *CHEMICAL NEWS*.

Support for Filtering Several Precipitates at Once.—E. Sauer (*Chemiker Zeitung*).—This instrument is intended for cases where the filtrates do not require to be preserved.

Separation of Small Quantities of Supernatant Liquids.—E. Drossaert (*Chemiker Zeitung*).—A small syphon drawn out and turned upwards like a hook at the end of the shorter limb.

Permeability of Caoutchouc Tubing for Carbonic Acid.—F. Kolbe.—A tube 77 c.m. in length and 8 m.m. in width, with sides 2 m.m. in thickness, allowed 6 c.c. of carbonic acid to escape hourly.

Application of Hydrogen Peroxide for Determining the Value of Chloride of Lime, Pyrolusite, and Permanganate.—G. Lunge (*Zeit. Angew. Chemie*).—This paper will be inserted at some length.

Standard in Acidimetry and Alkalimetry.—H. Heidenhain (*Chemiker Zeitung*).—The author recommends as standard potassium bitartrate.

Agent for Opening up Minerals.—C. A. Burghardt.—From the *CHEMICAL NEWS*.

Preservation of Sulphuretted Hydrogen Water.—Firemi (*Chemiker Zeitung*).—The author has bottles with glass capsules fused to the neck round the stopper. The capsule contains a layer of a mixture of glycerin and water 4 to 5 m.m. in depth, whilst a small glass bell covering the stopper dips into the capsule.

Separation and Determination of Nickel and Cobalt.—Constantine Kraus (*Mittheilungen aus dem Laboratorium der Universität Erlangen*).—A critique of the known methods which will be inserted successively.

Determination of Manganese in Iron and Steel.—L. Rürup.—Already noticed.

Determination of Camphor in Celluloid.—F. Foerster.—The object is decomposed by treatment with soda-lye, the camphor is driven off by distillation, separated from the distillate by means of measured quantities of benzol, in which the proportion of camphor is determined optically.

Determination of Value of Solutions of Mercuric Chloride, &c.—J. Bongartz.—The chlorine of an aqueous solution is determined volumetrically.

Optical Valuation of Quinine and Cinchonidine.—O. Hesse.—The author questions the applicability of the optical methods of De Vrij, Oudemans, and Koppo-schaar.

Determination of Alkaloids in Narcotic Extracts.—O. Schweissinger and G. Sarnow.—The authors dissolve 2 grms. extract in 8 c.c. water, add 2 c.c. ammonia, and shake up with a mixture of 15 parts chloroform and 25 parts ether.

Reaction of Morphine with Sulphuric Acid and Phosphates.—Vulpus.—If a few drops of a liquid containing at least $\frac{1}{2}$ m.grm. of a morphine salt is mixed with six drops undiluted sulphuric acid, a few c.grms. of sodium phosphate are added, and the capsule is heated over a flame with constant stirring, there appears a violet colour. On adding to the cold mixture water, drop by drop, it turns bright red, and finally a dirty green.

Examination of Manures, Cattle-Foods, and Soils.—Procedures adopted at the third general meeting of the Union of Agricultural Experimental Stations. The methods for sampling and analysis will be given in detail.

Determination of Mercury in Animal Tissues.—B. Ludwig and E. Zillner comminute the parts and boil them over an open fire with an equal weight of hydrochloric acid at 20° in a flask fitted with a Liebig's condenser until all the solids are dissolved. When the liquid

has cooled down to 60° a few grms. potassium chlorate are added in portions of $\frac{1}{2}$ gm. The cold liquid is filtered, the filter rinsed, and the entire liquid is repeatedly mixed with a few grms. of zinc-powder, whilst constantly stirring. From the dried mass the mercury is separated by a process of distillation.

Determination of Urea.—S. H. Smith.—(From the *Pharm. Journal*). Short notices follow on the detection of sugar in urine and in blood; of phenols in urine and of melanin in urine.

Distinction between Arsenical and Antimonial Spots obtained by the Process of Marsh.—G. Denigés.—From the *Comptes Rendus*.

The Colour Reactions of Strychnine.—C. L. Bloxam.—(From the *CHEMICAL NEWS*). For certain methods for the detection of strophantine and cocaine we refer to the original.

MISCELLANEOUS.

Examination of Glass.—F. Mylius (*Berichte Deutsch. Chem. Gesell.*).—The objects to be examined are carefully washed with water, next with alcohol, and then with ether, and whilst still moist with ether they are treated with a solution of eosine. To prepare this solution commercial ether is saturated with water by agitation, and 0.1 gm. of iodeosine is dissolved in every 100 c.c. The decomposability of the glass may be judged by the colouration produced.

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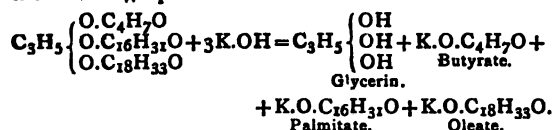
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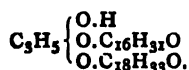
ON THE REACTION OF GLYCERIDES WITH ALCOHOLIC ALKALIES.*

By ALFRED H. ALLEN.

THE natural fats and fatty oils are commonly regarded as consisting, with a few exceptions (*e. g.*, sperm oil), of the glycerides of the fatty acids. It rarely, if ever, happens that a natural fat consists merely of a single glyceride, and there is good reason to believe that in many cases different fatty acid radicals occur in the same molecule. Butter-fat is a good illustration of this, for the butyric cannot be separated by any process of fractional solution from the less soluble glycerides. On saponification it yields butyric acid, and acids which are generally considered as being oleic and palmitic acid;† besides smaller amounts of arachidic, stearic, myristic, and lower acids of the stearic series. The result of saponifying a complex glyceride molecule containing the radicals of butyric, palmitic, and oleic acids, is shown by the following equation:—



By treating butter-fat with only one-half the quantity of alcoholic soda necessary for its complete saponification, and diluting the liquid with water, Dr. James Bell obtained an oil which solidified at 4° C., and on saponification yielded 88·1 per cent of insoluble fatty acids, but no butyric or other soluble fatty acid. This result agrees with the formation of a di-glyceride of the following character, though it is to be regretted that no determination of the glycerin was made:—

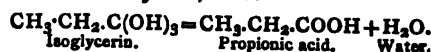


The products theoretically resulting from the saponification of natural fats and fatty oils, assuming them to have the constitution of triglycerides, will consist of from 94 to 96 per cent of fatty acids, and from 8·75 to about 13 per cent of glycerin, the usual proportion of the latter product being between 10 and 11 per cent.

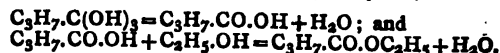
The Isoglyceride Theory.

In 1883, Messrs. J. A. Wanklyn and W. Fox enunciated a new theory of the constitution of natural fats (*CHEM. NEWS*, xlviii., 49; "British Association Reports," 1883, p. 470; *Analyst*, iv., p. 73). The theory, which was very shortly stated, was simply that the accepted view, that the fats are ethers of glycerin, is only partially correct, and that instances of a different kind of structure occur among the natural oils and fats. According to the authors of the theory, the fats are in part composed of ethers of isoglycerin or homologues of isoglycerin. To the wholly hypothetical compound, isoglycerin, these authors attribute the formula $\text{CH}_3\text{CH}_2\text{C}(\text{OH})_3$. This theoretical compound is assumed to exist only in its ethers, for

immediately on isolation it is imagined to be resolved into water and a fatty acid, thus:—



Of the existence of the isoglycerin with three carbon atoms absolutely no evidence has been attempted to be given; but the authors consider that proof of the existence in butter-fat of ethers of the next higher homologue is afforded by the formation of ethyl butyrate when the fat is treated with an amount of alcoholic potash insufficient for its complete saponification. The formation of the ethyl butyrate they attribute to the decomposition of an isoglycerin containing C_4 , this isoglycerin splitting up into butyric acid and water, and the nascent butyric acid reacting with the alcohol to form ethyl butyrate, thus:—



Wanklyn and Fox found that, under favourable circumstances, they could obtain from butter fat an amount of ethyl butyrate equivalent to fully 3 per cent of butyric acid, or about one-half of the total amount which can be isolated from saponified butter. Upon this single fact, coupled with a supposed serious deficiency in the amount of glycerin yielded when fats, and especially butter, are saponified, the authors erected their isoglycerin theory. But the reaction in question was some years since demonstrated by Mr. Hehner to be true also of synthetically prepared glyceryl butyrate: besides which, I believe, Messrs. Wanklyn and Fox have never published a single original experiment in support of their assertion that the proportion of glycerin yielded by saponification of butter and other fats exhibits any grave departure from the amount required by the accepted view of their constitution.

In view of this omission, the isoglycerin theory might well have been allowed to remain at rest had it not recently been reusucitated by Mr. Wanklyn in a wholly unaltered form. Thus, at a recent meeting of the Society of Chemical Industry (*Journal*, x., p. 93), Mr. Wanklyn stated that "The evidence of the existence of the isoglyceride was that reaction (*i.e.*, the formation of ethyl butyrate), and the fact that one did not really get the theoretical quantity of glycerin from butter."

Mr. Wanklyn considers that the formation of ethyl butyrate, on heating butter-fat with a limited quantity of alcoholic potash, proves the existence of an isoglyceride, the isoglycerin of which splits up into butyric acid and water, the acid reacting with the alcohol to form ethyl butyrate. He contends that if the butyric acid were a primary product of the saponification of an ordinary glyceride, instead of a secondary product of the decomposition of an isoglycerin, it would not form ethyl butyrate, but potassium butyrate. It is certainly a curious and interesting fact that ethyl butyrate should be formed under any circumstances, seeing that it is readily converted by caustic potash into alcohol and potassium butyrate. But it must be remembered that the essential condition of its formation in notable amount, prescribed by Wanklyn and Fox themselves, is the use of the alkali in quantity insufficient to saponify the whole of the butter fat employed. The whole argument derived from the reaction falls to the ground in the face of the fact, demonstrated some years since by Mr. Hehner under the very noses of Messrs. Wanklyn and Fox (*Analyst*, ix., 76), that butyric synthetically prepared by heating together butyric acid and glycerin, and thoroughly washing the product, develops abundance of ethyl butyrate when warmed with alcoholic potash!

The fact is that the reaction, which is regarded by Mr. Wanklyn as so anomalous, appears to be a perfectly normal and general one. Thus ethyl stearate may be actually prepared by boiling tristearin with a solution of sodium in absolute alcohol (Duffy), or by heating tristearin with small quantities of alcoholic potash (Bouis, *Compt. Rend.*, xlv., 35). Here, then, is the precise condition of success

* A Paper read before the British Association, Cardiff Meeting, 1891, Section B.

† Mr. J. A. Wanklyn believes butter fat to contain some 40 per cent of the glyceride of a peculiar acid, which he names aldehydic acid, having the formula $\text{C}_{16}\text{H}_{32}\text{O}_2$.

in obtaining ethyl butyrate applied by Bouis to prepare the higher homologue.

P. Duffy (*Journ. Chem. Soc.*, v., 363) also obtained amyl stearate by boiling tristearin with a solution of sodium in amyl alcohol, and amyl palmitate by precisely similar means. When in the reaction of stearin and palmitin with amylate of sodium the proportion of the latter was increased beyond one equivalent, the quantity of ether obtained diminished, "with a quantity of sodium which was certainly not less than two equivalents, no ether was obtained."

Duffy further observed that when free stearic acid was substituted for stearin in the foregoing reaction, no ether was produced.

Experiments on Acetin.

It appears, therefore, that the glycerides of stearic, palmitic, and butyric acids each yield abundance of the ethyl salts of these acids when heated with alcoholic potash. To complete the chain of evidence and study the reaction more thoroughly, I have recently made a series of experiments, in conjunction with Mr. David Homfray, on acetin, the glyceride of acetic acid.

Some acetin was prepared by heating together 5 parts of glycerin with 6 of anhydrous sodium acetate and 15 of acetic anhydride. The mixture was kept boiling for an hour, in a flask furnished with a reflux condenser. It was then treated with water, and sodium carbonate added till the reaction was permanently alkaline, when the liquid was shaken with ether, which was separated, and the acetin recovered by distilling off the solvent.

One gram. of the acetin thus prepared was distilled with 30 c.c. of alcohol and 0.5 c.c. of alcoholic potash containing 80 grms. of caustic potash per litre. The distillate, which smelt strongly of acetic ether, was heated on the water-bath for half an hour with 10 c.c. of the same alcoholic potash solution (=11.8 c.c. normal KHO), and the excess of alkali titrated back with standard hydrochloric acid and phenol-phthalein in the usual way. From this result we calculated the weight of acetic acid volatilised as acetic ether. The residue in the retort was treated with more alcohol and another 0.5 c.c. of alcoholic potash, the liquid distilled, and the distillate saponified as before. The following results were obtained, operating on 1 gram. of acetin in each case:—

	Alcoholic KHO employed. C.c.	Acetic acid in distillate. Per cent.	= Acetin. Per cent.
a. First distillate ..	0.5	53.4	65.12
Second " ..	0.5	17.4	21.22
Total ..	1.0	70.8	86.34
b. First distillate ..	0.2	43.8	53.42
Second " ..	1.0	26.4	32.19
Total ..	1.2	70.2	85.60

The theoretical yield of acetic acid, supposing the whole of the substance employed to be pure triacetin and the conversion into ethyl acetate to have been complete, would be 0.826 gram. against 0.708 and 0.702 gram. actually produced.

A fresh quantity of acetin was next prepared, and an experiment made to ascertain if it volatilised with vapour of alcohol. 1.0848 gram. of acetin was distilled with 50 c.c. of alcohol, the distillate and residue both saponified, and the acetin calculated as before. In the distillate only 0.015 of acetic acid was found, while the residue contained 0.752 gram., the sum of the two being 0.767 gram. This result shows that the extraordinary results previously obtained were not due to actual volatilisation of acetin as such. The total yield of acetic acid is below the theoretical amount (0.826 gram.), doubtless owing to the presence of mono- or diacetin in the material employed. That it was not due to any error of experiment was proved by saponi-

fying a known weight of the acetin with excess of alcoholic soda ($\frac{N}{5}$ normal) under a reflux condenser, and ascertaining the alkali consumed in the reaction by titration with standard acid and phenol-phthalein in the usual way. A yield of 76.03 per cent of acetic acid was obtained, as against 76.7 recorded above.

Another experiment was then made by distilling 1.135 gram. of the same specimen of acetin with 1.0 c.c. of $\frac{N}{5}$ normal soda and 30 c.c. of alcohol. The distillate was saponified with a known quantity of the same alcoholic soda, and titrated back with hydrochloric acid as usual. The residue in the retort was again distilled with alcohol and 1.0 c.c. of the same soda solution, and this treatment was repeated once more. The following are the figures obtained:—

	Alcoholic NaHO employed. C.c.	Acetic acid in distillate. Per cent.	= Acetin. Per cent.
First distillate ..	1.0	32.19	39.02
Second " ..	1.0	26.22	31.97
Third " ..	1.0	11.00	13.41
Total ..	3.0	59.41	84.40

The volume of the caustic soda solution requisite to completely saponify the 1.135 gram. of acetin employed would be 50 c.c. Hence 1 c.c. of the alkaline solution is chemically sufficient to saponify only about one-fiftieth of the acetin used, and yet it causes the conversion of 39 per cent of it into acetic ether, while 3 c.c. converts 84.4 per cent.

Further experiments showed that the employment of a larger proportion of alkali diminished the yield of acetic ether; thus with sufficient caustic soda to saponify 12.7 per cent of the acetin used, 85.2 per cent of the total acetic acid passed into the distillate as ethyl acetate. This, with the 12.7 remaining in the retort as sodium acetate, leaves only 2.1 per cent unsaponified or otherwise to be accounted for. In another experiment, in which the alkali used was equivalent to 39.8 per cent of the acetin, the amount converted into acetic ether was 52.4 per cent, leaving 7.8 per cent unaccounted for.

In all cases the distillates were found to be neutral to phenol-phthalein, showing that no free acetic acid had distilled over. The residues in the distilling flasks were always found to be slightly, but distinctly, acid to phenol-phthalein, a fact which proves that the whole of the alkali employed invariably entered into reaction, and that some reaction occurred resulting in the production of free acetic acid. Hence it appears probable that the first action of the alkali on the acetin is to effect its hydrolysis, with formation of glycerin and free acetic acid. A portion of the latter then reacts with the alkali to form sodium acetate, while the greater part reacts with the alcohol to form ethyl acetate; but a small proportion of the acetic acid fails to enter into this latter reaction, and hence remains in the free state in the distilling flask. Why the soda should effect the hydrolysis of a much larger amount of acetin than it can chemically react with is not clear; but the behaviour of soda is evidently similar to that of lime, magnesia, and oxide of zinc, very small amounts of which (2 or 3 per cent) are found to very greatly facilitate the hydrolysis of fats by super-heated steam, and are largely employed with this object.

A few supplementary experiments deserve mention. 1 gram. of anhydrous sodium acetate was distilled with 50 c.c. of alcohol, the distillate boiled with alkali, and titrated back with standard acid, when it was found that no acetic ether had been formed. A mixture of acetin, alcohol, and anhydrous sodium acetate gave a small yield of acetic ether. It seemed possible that the result might be due to the presence of alkali in the sodium acetate. Hence the experiment was repeated by dissolving sodium acetate in alcohol, dropping in acetic acid till the alkaline

reaction to phenol-phthalein disappeared, then adding acetic acid and distilling as before. Acetic ether equivalent to 1.36 and 1.50 of the acetic taken was found in the distillate. This is no more than was obtained by distilling acetic acid and alcohol together.

The foregoing results appear to be so far-reaching in their consequences that I propose to investigate the subject more systematically than I have hitherto been able to do.

Duffy determined the glycerin produced by the saponification of the stearin he employed. The method of estimation consisted in evaporating the neutralised liquid resulting from the saponification nearly to dryness at a steam-heat, adding dry potassium carbonate, extracting the glycerin with absolute alcohol, filtering the solution, and evaporating the filtered solution in a vacuum until the residue was of constant weight. The glycerin thus found was corrected by the deduction of the ash left on ignition. By this process, which is likely to give low results, Duffy obtained 8.94 per cent of glycerin in two experiments, the theoretical yield from pure stearin being 10.34 per cent, a figure which does not leave much margin for the suggestion that the ethyl and amyl stearates were derived from an isoglycerin, which under the circumstances would have to be the member with 18 carbon atoms!

The process of estimating glycerin employed by Duffy was substantially the same as that described by Chevreul in 1823, by which the chemist isolated the following proportions of ash-free glycerin:—Human fat, 9.66 per cent; pork, 8.82; beef, 8.60; mutton, 8.00; butter fat, 11.85; porpoise oil, 14.00. These results, with the exception of the two last, are sensibly below the theoretical yield, as might be expected from the process employed. Further, the statement made by Mr. Wanklyn that manufacturers never obtain more than 5 per cent of glycerin on saponifying fats, is contrary to the experience of some of the largest firms, who recover 7.5 to 8 per cent, and take no notice of the considerable loss of glycerin by evaporation during the process of concentration, besides which the process of saponification is often far from complete.

To come to more recent determinations of glycerin in fats, Mr. Hehner has published the following figures, obtained by boiling the leys from the saponification with a dilute acid solution of potassium bichromate, and ascertaining the excess of oxidising agent by titration with a ferrous salt (*Analyst*, xii., 44).

Now this process is not open to the objection which has been raised against some, for it has recently been stated by a coadjutor of Mr. Wanklyn (*Journ. Soc. Chem. Ind.*, x., 204) that dilute chromic acid mixture remains practically unchanged when boiled with butyric acid, and further (*Analyst*, xvi., 30), that butyric acid is the only soluble non-volatile fatty acid to be detected in the glycerin mother-liquor obtained by the saponification of butter fat.

The following are figures obtained by Mr. Hehner by the bichromate titration process:—

Fat.	Glycerin.
Olive oil	10.26 per cent.
Cod-liver oil	9.87 "
Linseed oil	10.24 "
Margarine	10.01 "
Butter fat	12.40 "

As already pointed, it is a curious fact that the authors of the isoglyceride theory have not, to my knowledge, published any experiments in support of their assertion that butter, tallow, and other fats yield on saponification little more than half the theoretical proportion of glycerin. This is the more curious since a valuable method of determining glycerin in fats was originally suggested by Mr. Wanklyn and further worked out by Mr. Fox (*Oil and Colour Journ.*, v., 1402; *CHEMICAL NEWS*, liii., 15) and Benedikt and Zeigmondy (*Chem. Zeit.*, ix., 975; *Analyst*, x., 206). The method is based on the oxidation of the glycerin by treatment with permanganate in pre-

sence of excess of caustic alkali, whereby it is converted into oxalic acid, carbon dioxide, and water, in accordance with the equation, $C_3H_8O_3 + 3O_2 = C_2H_2O_4 + CO_2 + 3H_2O$. The excess of permanganate is destroyed by a sulphite, the filtrate acidulated with acetic acid, and the oxalate precipitated as a calcium salt.

This process has been very fully investigated in my laboratory by Mr. J. C. Belcher, and proved to give very accurate results in the absence of foreign bodies yielding oxalic acid by oxidation. Alcohol is one of these, and hence, to avoid all risk of its presence, I have described a method of saponifying the substance with aqueous potash (*Analyst*, xi., 52; "Com. Org. Analysis," ii., 290). This modification and careful proof by experiment that oxalic acid is not acted on by permanganate in strongly alkaline solution, is the extent of my responsibility for the process in question (*Jour. Soc. Chem. Ind.*, x., 204).

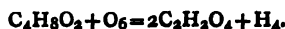
Benedikt and Zeigmondy, however, proved by experiment that the soluble fatty acids of oils, such as acetic, butyric, caproic, &c., do not, on treatment with alkaline permanganate, yield any acids the calcium salts of which are precipitated from acetic solutions, and hence are liable to be mistaken for calcium oxalate. The higher fatty acids of the stearic series are insoluble in water, and hence would not in any case interfere. On the other hand, certain acids of the acrylic or oleic series, and possibly oleic acid itself, yield oxalic acid by oxidation with permanganate. The higher acids of the oleic series are, however, insoluble in water, and the lower are not known to occur in fixed oils under normal conditions. Under certain circumstances, however, the method is wholly invalidated, as I found when attempting to apply it to the examination of oxidised linseed oil.

The following tabulated statement of results obtained by the alkaline permanganate process of estimating glycerin is taken from vol. ii. of my "Commercial Organic Analysis," page 33:—

Kind of Fatty Oil.	Glycerin per cent.	
	Benedikt and Zeigmondy.	Allen.
Northern whale oil		11.96
Porpoise oil		11.09
Menhaden oil		11.70
Lard		10.83
Tallow	9.9—10.0	—
Butter fat	10.2—11.6	11.06
Olive oil	10.1—11.4	—
Linseed oil	9.4—10.0	9.39
Castor oil		9.13
Cocoa-nut oil	13.3—14.5	12.11
Palm-nut oil		11.70
Palm oil (containing much free acid)		9.71

Behaviour of Butyric Acid with Alkaline Permanganate

The applicability of the alkaline permanganate process to the estimation of the glycerin from butter has been recently denied by W. Johnstone (*CHEMICAL NEWS*, lxi., 111; *Analyst*, xvi., 49; *Jour. Soc. Chem. Ind.*, x., 204) on the ground that butyric acid itself yields oxalic acid on treatment with alkaline permanganate in the manner described by Benedikt and Zeigmondy for the estimation of glycerin. The same authority states (*Analyst*, xvi., 30) that butyric acid is the only soluble non-volatile acid he could detect in the glycerin mother-liquor from the saponification of butter, and he also states that the oxalic acid yielded is equivalent to from 11.7—12.23 per cent of glycerin (*Jour. Soc. Chem. Ind.*, x., 93). The effect of alkaline permanganate on butyric acid is stated to be to oxidise it to oxalic acid in accordance with the following somewhat eccentric equation (*CHEMICAL NEWS*, lxi., 111; *Jour. Soc. Chem. Ind.*, x., 204):—



Dr. William Johnstone, the discoverer of this reaction, quotes two experiments on pure butyric acid by which he obtained amounts of oxalic acid corresponding to 93.64 and 94.07 per cent of the butyric acid taken. This result is of so remarkable a nature, and so completely opposed to the experience of Benedikt and Zsigmondy and all previous observers, that one is disposed to receive it with some reserve, especially as the same observer recently published experiments (*Analyst*, xvi., 26), according to which tallow requires 23 per cent of caustic potash (KHO) for its saponification, against 19.3—19.8 per cent as the united experience of numerous other observers; that butter fat requires about 27 per cent of potash against the general experience of 22.1—23.3 per cent; and detailing other analytical results of an equally remarkable character.

As, however, the observer in question makes the distinct assertion, as the result of experiment, that butyric acid is oxidised to oxalic acid by alkaline permanganate, and hence that the estimation of glycerin in butter by the same process is invalidated, and considerable support thereby given to Mr. Wanklyn's isoglyceride theory (*Jour. Soc. Chem. Ind.*, x., 204), I have thought it right to ascertain by actual experiment whether the statement in question had any foundation in fact. That it was erroneous was already rendered extremely probable by Mr. Hehner's failure to obtain any trace of oxalic acid from butyric acid by treatment with permanganate (*Analyst*, xvi., 49).

In order to settle the point in question beyond the possibility of further cavil, 20 grms. of butter fat were saponified by heating it for six or eight hours to 100° C. in a closed bottle with a solution of 8 grms. of caustic potash in 50 c.c. of water. The soap obtained was dissolved in hot water, and decomposed by dilute sulphuric acid in quantity sufficient to convert the potash into KHSO_4 . The liquid was then allowed to become cold and poured off through a filter from the cake of insoluble acids. The latter was washed by boiling with water, the washings when cold being filtered and added to the main solution. This solution, containing the glycerin and soluble fatty acids resulting from the saponification, was then distilled to a small bulk, water added, and the liquid again distilled to a small volume.

The distillate was then oxidised by alkaline permanganate in the usual way. The reduced and filtered liquid gave no trace of precipitate when acidulated with acetic acid and treated with calcium chloride, showing that no oxalic acid had been formed from the butyric acid, and that no glycerin had distilled over.

The residual liquid remaining in the distilling flask was divided into four equal portions. Nos. 1, 2, and 3 were oxidised by respectively a slight excess, a moderate excess, and a large excess of alkaline permanganate, by which quantities of oxalic were formed equivalent respectively to a production of 11.12, 11.52, and 11.78 per cent of glycerin by the saponification of the butter fat. The fourth portion of liquid was exactly neutralised by caustic potash, concentrated, cooled, and filtered from the potassium sulphate which crystallised out. The filter was washed with alcohol, and more alcohol added to the filtrate as long as a precipitate was produced. The liquid was filtered and evaporated on the water-bath till the residue was nearly constant in weight. The residue, which was syrupy and had the characters of glycerin, was ignited and the ash deducted from the weight previously observed. A direct determination of the glycerin by weight in this manner showed 11.22 per cent.

Other estimations of glycerin by the same process, but employing 20 grms. (instead of 5 grms.) of butter fat gave 10.77, 11.53, and 12.15 per cent of ash-free glycerin.

In another experiment 20 grms. of butter fat was saponified with aqueous potash, the soap decomposed with acid, and the acid liquid divided into two equal portions, A and B.

A was distilled to a small bulk as before, and the residue in the flask divided into two equal portions.

No. 1 showed by oxidation with alkaline permanganate 11.52 p.c. of glycerin.

No. 2 gave Mr. Hehner by the bichromate oxidation-method 11.83 p.c. of glycerin.

B was divided into two equal parts without previous distillation to separate butyric acid.

No. 3 showed with alkaline permanganate 10.86 per cent of glycerin.

No. 4 was lost.

The foregoing experiments were made in my laboratory by Mr. D. Homfray, to whom my best acknowledgments are due. The experiments appear to prove:—

1. That butyric acid does not yield oxalic acid when oxidised by alkaline permanganate in the manner prescribed by Benedikt and Zsigmondy.

2. That the amount of oxalic acid formed by oxidising by alkaline permanganate the soluble products of the saponification of butter, is not greater when the oxidation is effected in presence of the butyric acid than when that acid is previously removed by distillation.

3. That the oxalic acid produced by the permanganate treatment corresponds to a formation of 11 to 12 per cent of glycerin from the butter fat saponified.

4. That this result is fully confirmed by actual isolation and weighing of the glycerin resulting from the saponification.

5. That there is no foundation for the isoglyceride theory so far as butter fat is concerned.

A NEW QUANTITATIVE SEPARATION OF MANGANESE AND ZINC.

By PAUL JANNASCH and J. F. MCGREGORY.

THE process depends on the ready and complete conversion of the former metal into insoluble manganese hyperhydroxide by the action of hydrogen peroxide in an alkaline solution, whilst compounds of zinc, if present, remain unaffected. Carnot was the first who precipitated manganese salts alone by the above reagent, and thus determined their manganese quantitatively.

As one of the writers made numerous preliminary experiments more than two years ago on the oxidising action of hydrogen peroxide, and in developing his new method for the determination of sulphur in inorganic sulphides, found that it was a remarkably efficient oxidising agent, he thought it well not to delay any longer to institute a series of quantitative separations by means of hydrogen peroxide. The first of these results, the separation of zinc and manganese, executed in concert with Prof. McGregory, is here communicated.

In our first experiments we proceeded with solutions of the mixed sulphates acidified with dilute hydrochloric acid, adding next a moderate excess of concentrated ammonia, and then heating the precipitation with hydrogen peroxide for some time on the water-bath. Considerable quantities of zinc oxide were regularly found mixed with the precipitate of manganese. In one case where the precipitate had stood covered on the water-bath for more than four hours, the manganese separated was found to contain 0.0822 gm. ZnO (the quantities employed having been 0.5380 gm. $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$, and 0.5602 gm. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$). That precipitation of zinc was occasioned by the expulsion of the excess of ammonia on the water-bath was learnt from the solutions filtered off from the manganese precipitate, which, on evaporation, soon be-

came turbid by the separation of a white flocculent deposit which was subsequently re-dissolved.

As we afterwards heated on the water-bath for a very short time only, the results obtained were considerably better, so that on the average the proportion of manganous oxide was found too high by 2.5 per cent, which excess could be reduced by 0.5 per cent by washing the precipitate with dilute ammonia. The results obtained became perfectly satisfactory only when we considerably increased the proportion of the ammonium chloride and ammonia in the liquid to be precipitated, and proceeded finally exactly as follows:—A mixture of 0.5 gm. manganese sulphate and 0.5 gm. zinc sulphate were dissolved in 75–100 c.c. of water in a capsule of Berlin porcelain capable of conveniently holding 600 c.c., and the solution was acidulated with a little dilute hydrochloric acid. A considerable quantity of a 15–20 per cent solution of sal-ammoniac (at least 100 c.c.) was added, and lastly the liquid was made strongly alkaline by the addition of 60–100 concentrated ammonia, when no brownish colouration of manganese hydroxide must appear. The solution thus prepared and covered with a glass capsule is immediately mixed with an excess (50–60 c.c.) of pure hydrogen peroxide (*Hydrogenium peroxidatum puris* from H. Trommsdorff, of Erfurt, and perfectly free from barium chloride), which at once completely precipitates all the manganese. The mixture is then heated for 10–15 minutes on a boiling water-bath until the precipitate subsides perfectly, when it is collected on a capacious filter. Any residue adhering to the porcelain is removed by means of a goose-feather, suitably trimmed, rinsed out of the capsule by means of hot water and a little ammonia. The precipitate is washed with boiling water, slightly ammoniacal, and at last with hot water alone, until a drop of the filtrate, if evaporated on platinum foil, leaves no residue. The precipitate of manganese may be incinerated while still moist in a platinum or porcelain crucible, and ignited in the blast flame until the weight is constant. A repetition of the precipitation is quite superfluous, and it is not necessary to dissolve the precipitate in hydrochloric acid in order afterwards to precipitate the manganese as a carbonate.

For determining the zinc in the filtrate which has thus been freed from carbonate there is the choice of two methods. In the former, the boiling ammoniacal solution is precipitated with ammonium sulphide, and the precipitate of zinc sulphide is heated for an hour on the water-bath and filtered.

As the precipitate of zinc sulphide cannot be washed without inconvenience, owing to its clogging the filter and running through turbid, it is better to pass only the liquid in the beaker through the filter, then to return the latter with the unwashed precipitate into the beaker, and re-dissolve the precipitate in dilute hydrochloric acid with the aid of heat, so that the precipitation of zinc may be effected by sodium carbonate in presence only of a trifling quantity of ammonium salt. It must be remembered that zinc carbonate if thus precipitated may be contaminated with a little silica.

The second method is equally accurate and more rapid. The solution of zinc is evaporated to dryness in a large platinum capsule on the water-bath (stirring towards the end is not necessary); the residual saline mass is heated for about an hour on an air-bath to 125–150°, and the ammoniacal salts are driven off by heating more strongly on an asbestos capsule over the gas flame. The saline masses left adhering to the sides of the capsule are pushed down, to the bottom by means of a stout platinum wire. The expulsion of the ammoniacal salts by direct heating over the naked flame is not admissible, as particles of zinc might be lost. The non-volatile residue is dissolved in hot water and a couple of drops of hydrochloric acid, the solution is filtered, and the filtrate, whilst boiling, is precipitated with sodium carbonate.

The authors are already in a position to assert that manganese, nickel, and probably cobalt, may be separated

in a similar manner. They are further studying the behaviour of the alkaline potassium cyanide solutions of cobalt, nickel, and manganese with hydrogen peroxide.—*Journ. für Prakt. Chemie.*

CONTRIBUTIONS TO MICRO-CHEMICAL ANALYSIS.*

By H. BEHRENS.
(Concluded from p. 174.)

L.—Tellurium.

1. MAGNESIUM throws down, from acid solutions of tellurium dioxide, films and scales of tellurium which appear of a dark greyish brown by transmitted light. Selenium is masked, even if present in considerable quantity. On the other hand, arsenic masks tellurium. The limit of the reaction is at 0.006 m.grm. Te.

2. Cæsium chloride precipitates from solutions of tellurium dioxide a hydrochloric acid yellow octahedra of 10–30 micro. Chloro-tellurite is distinguished from chloro-platinate by the size of its crystals and its behaviour with water. The crystals are rendered turbid by water, from which they cannot be re-crystallised, though they can from hydrochloric acid. Potassium iodide covers them black. The limit of the reaction is at 0.0003 m.grm. Te.

3. Potassium iodide occasions no change in alkaline solutions of tellurium dioxide. On the addition of hydrochloric acid a yellow and brown colouration appears, and there are deposited opaque rhombs, hexagons, and rods of 10–20 micro., which appear of reddish brown by reflected light. The reaction has its limits at 0.0006 m.grm. Te, and in presence of bismuth it is worthless.

From solutions containing selenium and tellurium, potassium iodide precipitates first tellurium iodide and afterwards red selenium iodide. If tellurate and selenite were in solution, selenium iodide is thrown down only after heating with hydrochloric acid. Selenium iodide may also be recognised by sublimation, as it is volatilised at a lower temperature than tellurium tetraiodide.

LI.—Molybdenum.

1. Sodium phosphate, after supersaturation with nitric acid, throws down yellow phospho-molybdate from solutions of molybdic acid in potassa or ammonia. Compare Potassium 2. Care must be taken that there is no excess of sodium phosphate in the liquid as it has a solvent action upon the insoluble phospho-molybdates. By proceeding cautiously 0.0001 m.grm. of Mo can be recognised in this manner. Thallous phospho-molybdate has a more intense colour, and forms smaller crystals than the potassium salt. It adheres firmly to the glass, and is therefore suited for separating and concentrating molybdenum, the rather as it can be converted into the compound mentioned under No. 2 of Potassa or Soda.

2. Thallous sulphate determines, in solutions of molybdic acid which contain free alkali, the separations of colourless, reflecting, hexagonal leaflets of 30–60 micro., which are so thin that by reflected light they show bright interference colours from blue-grey of the first order to green of the second. By the side of the leaflets and upon them there appears sometimes an elegant network of thin reflecting rods. In both cases we have probably to do with Oettinger's molybdate, Tl_2MoO_4 . The limit of this fine reaction is at 0.000033 m.grm. Mo; the limit of immediate precipitation is at a 5000 times dilution of molybdic acid.

It is most convenient to place a granule of thallous sulphate in a solution which contains 0.1 per cent of molybdic acid and a small excess of caustic soda. The leaflets form then a fringe round the reagent. They are

soluble in hot water, but are not improved by re-crystallisation. Nitric acid destroys them rapidly, and if phosphoric acid is present yellow phospho-molybdate is deposited. On the other hand, thallous phospho-molybdate is converted by caustic soda into the compound here described.

LII.—Tungsten.

1. The yellow colour of precipitated tungstic acid appears most distinctly when the white hydrate is heated with hydrochloric acid. The most essential condition is a compact state of the precipitate. Light flakes and fine dust assume merely a yellowish tint. On this account the precipitate does not succeed with less than 0.01 m.grm. WO_3 . If it is not practicable to distinguish the yellow colour, the unequal solubility of molybdic and tungstic acids in nitric acid may serve for isolating and recognising the latter compounds. In this manner we may separate 0.002 m.grm. WO_3 . It is repeatedly evaporated down with strong acid, and then extracted in hot dilute acid. The limit of precipitation is at 0.0016 m.grm. W.

2. Sodium phosphate throws down from solutions of potassium and sodium tungstate, on the addition of an excess of nitric acid, colourless crystals of phospho-tungstate agreeing in form and shape with those of the phospho-molybdates. In solutions containing both molybdenum and tungsten there appear mixed crystals, the colour of which depends on the proportion of molybdenum. The limit of the reaction is at 0.00012.

3. Thallous sulphate gives, in alkaline solutions of tungstic acid, crystalline leaflets which may extend to 400 micro., but are in other respects exactly similar to those of thallous molybdate. If heated with nitric acid and sodium phosphate they are converted into colourless phospho-tungstate. The limit of the reaction is at 0.00008 m.grm. W.

LIII.—Uranium.

1. Sodium acetate precipitates, from neutral and faintly acid solutions of uranium, light yellow tetrahedra of uranyl acetate, which have been already mentioned under Sodium 1. The limit of instant reaction is between 1 and 0.5 per cent of uranyl acetate. Beyond this limit the reaction may be masked by other crystalline salts. In solutions which contain only uranium salt the reaction may extend to 0.0006 m.grm. U.

2. Thallous sulphate effects, in ammoniacal solutions of uranyl carbonate, the separation of clear pale yellow rhombs of 30–70 micro. in length. They display strong polarisation and right extinction. This reaction loses nothing of its distinctness if the uranyl salt is diluted 5000 times. Sodium carbonate may be used instead of the ammonium carbonate, but the rhombic crystals are the less simple and well developed. The limit of this reaction is at 0.0001 m.grm. U.

LIV.—Chlorine.

1. Thallous sulphate precipitates, from solutions of chlorides, small, colourless, strongly refractive cubes. Compare Thallium 1. Instead of thallous sulphate, lead acetate may be used, but the sensitiveness is then reduced to 0.0005 m.grm. Cl, and the long spiculae of lead chloride are not particularly characteristic. With thallous sulphate 0.0001 m.grm. chlorine may be recognised.

2. Silver nitrate throws down a curdy precipitate of silver chloride, which may be obtained in crystals by solution in ammonia or in hot hydrochloric acid. Compare Silver 1. The limit of the reaction is at 0.00005 m.grm. Cl.

3. Platinic sulphate renders the reaction by twenty times more sensitive. We test first with thallous sulphate, and if no reaction ensues we add platinic sulphate. Excess must be avoided, so as not to obtain crystals of double sulphates. Compare Thallium 3. The reaction detects 0.00004 m.grm. Cl.

4. If potassium sulphate or nitrate is used along with

platinic sulphate we obtain no greater sensitiveness than with salts of lead, but there are formed large crystals of potassium platinum chloride (compare Potassium 1), and the possibility of simultaneously detecting chlorine and bromine. (See Bromine.)

LV.—Bromine.

1. The reagents 1, 2, and 3 for chlorides give with bromides reactions which can only be distinguished from those described under Chlorine 1, 2, and 3, by the smaller size of the crystals. The limit of the reaction with thallous sulphate is 0.00016 m.grm. Br; with silver nitrate and ammonia, 0.00005 m.grm. Br; with thallous sulphate and platinic sulphate, at 0.00006 m.grm. Br.

2. With platinic sulphate and potassium nitrate we obtain, in solutions of bromides, orange-red octahedra of potassium platinum bromide *prior* to the appearance of the platinum chloride, which chiefly crystallises out at the margin of the drop. Here also an excess of the reagents must be avoided. The limit of the reaction is 0.00024 m.grm. Br. Instantaneous reaction is obtained down to 0.3 per cent potassium bromide.

3. If a little gold chloride is added to a solution containing not too little bromide, and if a granule of thallous sulphate is added, bromo-aurate crystallises out first. Solutions with 1 per cent potassium bromide yield an orange-red powder, which dissolves on heating. At the margin of the drop massive orange prisms then crystallise out. The heating must not be pushed too far, and caution must be used in the addition of the gold chloride in order to obtain as little chloro-aurate as possible. The limit of the reaction is at 0.0007 m.grm. Br; the limit of instantaneous action is at 3.0 per cent potassium bromide.

4. If we place in a liquid containing a bromide a few granules of starch, acidulate with sulphuric acid, and add finally a little potassium nitrite, the starch granules assume a colour varying from light yellow to orange-yellow. With solutions which contain less than 0.2 per cent of potassium bromide we have to wait some minutes for the appearance of the colour. In this case it is advisable to cover the preparation with a flat watch-glass. As a matter of course caution must be used with the addition of the nitrite if chlorides are present. The reaction is exceedingly characteristic, but unfortunately not as sensitive as it might be desired. The limit lies at 0.02 m.grm. Br.

LVI.—Iodine.

1. Thallous sulphate and silver nitrate give yellow precipitates in solutions of iodides, which cannot readily serve for detecting iodine in presence of bromine. In case of need thallous bromide can be extracted by boiling in water, and silver bromide by treatment with ammonia in the cold. The limit of the precipitation for thallous sulphate is at 0.00017 m.grm. I; silver nitrate is not more sensitive, as the solution of silver iodide in ammonia does not yield characteristic crystals.

2. Palladium nitrate occasions in solutions of iodides, even if very dilute, a flocculent black-brown precipitate. Compare Palladium 1. The limit of the reaction is 0.0001 m.grm. I. If bromine is present palladium chloride is used instead of the nitrate.

3. Platinic sulphate colours solutions of iodides a vinous red, and separates out black, pulverulent, platinum iodide. If potassium salts are present the separation of platinum iodide may not take place; there appear octahedra of platinum-potassium iodide, resembling graphite in colour, and of the same size as those of the chloro-platinate; they appear first, *before* the orange-red crystals of the bromo-platinate. The limit of the reaction is at 0.0002 m.grm. I; the limit of immediate reaction is at the 800-fold dilution of potassium iodide.

4. Mercuric chloride precipitates iodides of a scarlet colour. The reagent is characteristic and convenient, as an excess of the reagent is not injurious. Compare

Mercury b, 1. The limit of the reaction is 0.0002 m.grm. 1.

5. Starch is coloured by free iodine an intense blue; the process is the same as that described under Bromine 4. If much sulphuric acid is added the colour of the iodised starch grows paler after some time, and becomes a vinous red. The limit of this very characteristic reaction is at 0.00017 m.grm. 1. If bromine is present along with iodine, the colour of the starch occasioned by the latter may be easily masked. The blue colour is alone perceptible, and it must be destroyed before the reaction of the bromine is visible. This can be easily effected by the addition of hydrochloric acid and a particle of potassium chlorate. In the vicinity of the latter the starch granules are decolourised, or, if bromine is present, turned yellow to orange. Subsequently the yellow colour disappears here, but becomes more distinct at a greater distance.

LVII.—Fluorine.

1. Sodium chloride is to be recommended as a precipitant whenever it is necessary to distil off fluorine as silicon fluoride. Compare Silicon 1. This limit of the reaction is then at 0.002 m.grm. F. Fluoriferous silicates which are not decomposed by sulphuric acid are prepared by fusion with soda and evaporation with acetic acid. If no distillation is needed the limit is at 0.00004 m.grm. F.

2. Barium salts yield a silico-fluoride less characteristic in form (compare Barium 2), but react three times more sensitively than sodium chloride. In the most favourable case the limit with barium chloride is 0.000015 m.grm. F.

ON A COMBINATION OF WET AND DRY METHODS IN CHEMICAL ANALYSIS.*

PART I.

By W. E. ADENEY, F.I.C., Assoc.R.C.Sc.I., Curator, Royal University of Ireland; and T. A. SHERGOG, A.I.C., Assoc.R.C.Sc.I., Assist. Chemist, Royal College of Science, Dublin.

(Continued from p. 175).

Details of Manipulation.

The Charcoal Support.—The pieces should be from 12 inches to 18 inches in length, and from 1½ inches to 2 inches in diameter, and must be tolerably free from fissures. Our first experiments were made with charcoal of a very fair quality got from Messrs. Griffin and Son, of London. Later on, some of excellent quality was obtained from Messrs. Harrington Bros., of Cork.

The cavity into which the substance is to be introduced should be bored in the end of the stick of charcoal, and its size and shape are of importance. In shape it should be conical, the sides being slightly curved. The dimensions most convenient for the quantities we dealt with were—diameter, 1½ inches; greatest depth, 1½ inches. If the cavity be much larger or smaller than this, the charge cannot be worked about in the proper manner. The ratio of diameter to depth should be attended to, for if the hole be too deep in relation to its diameter, the flame will be blown back, and the charge cannot be properly heated.

The Source of Heat.—In our earlier experiments a lamp which burnt solid paraffin was used. This had the advantages of being very portable and not likely to get out of order. Later on an ordinary paraffin oil lamp was employed; but, although either of these lamps will answer perfectly, we found that when coal gas is procurable it is by far the most convenient source of heat. It can be burnt at the end of a flattened tube, and if the tube be pivoted so that it can rotate in a vertical plane it will be found of advantage in dealing with easily oxidisable metallic beads, as will be explained later.

The blowpipe used was an ordinary mouth blowpipe, furnished with a platinum jet, and fixed in a clip on a

retort-stand. An indiarubber hand blower was used for obtaining the blast.

The borax used was fused in a platinum dish and powdered. It should be kept in a dry and well-stoppered bottle.

The silver was at first fused in the form of nitrate, but the troublesome deflagration which took place when this salt was heated soon led to its use being discontinued. Silver chloride, mixed with the substance and borax before fusion, was next tried, and was found to work very satisfactorily. Subsequently it was found that with substances of a certain type, the most satisfactory results were obtained when the substance and fluxes were first fused together in a shallow cavity in charcoal, the oxidising flame being employed. When fusion was complete the mass was allowed to cool, transferred to a cavity of the usual size and shape in a fresh piece of charcoal, the silver added in the form of wire or in a button, and the fusion continued in the reducing flame. Experiments were also made in which silver oxide was used instead of silver chloride, but no advantage was apparent. In some cases, when dealing with metals which form infusible alloys with silver, lead was added, either as litharge or as metal. The results obtained were not satisfactory, but this requires further working out.

The form in which the silver should be added depends on the nature of the substance. If the substance consists mostly of compounds of lead, bismuth, copper, arsenic, antimony, or tin, silver chloride should be employed, and should be mixed with the substance and borax before the fusion. If, however, the substance consists principally of difficultly reducible oxides or oxides of nickel or zinc, then metallic silver, added after fusion, is best.

In some cases the substance and fluxes were fused together in a shallow cavity, using the oxidising flame; cooled, powdered in an agate mortar, then mixed with silver chloride, and again fused. This is very troublesome, and the employment of the silver as wire was found to give quite as good results.

The sodium carbonate used was the ordinary dried and powdered material. After a great number of experiments its employment was discontinued, except when dealing with siliceous substances, as no advantage seemed to attend its use with other bodies.

Quantities.—The most convenient quantities to work upon generally are 3 decigrams of substance, and 12 decigrams of borax. These quantities yield beads which can be easily worked before the blowpipe in the necessary manner, in a cavity of the dimensions given above. The proportion of borax may be varied within reasonable limits (from two to six times the weight of substance taken) without injuriously affecting the fusion. In dealing with a body containing very large proportions of nickel or zinc, not more than 1 decigram of the substance should be taken.

While the fusion is proceeding, the charge must be worked round and round the cavity, the metal bead being made to run round the glass, and pick up the metals as reduced. When finished the whole charge may be allowed to sink to the bottom of the cavity, the metal bead being under the glass. This somewhat protects the metals from oxidation.

The fusion must be cooled most carefully in an atmosphere of coal gas (by directing a stream of gas into the cavity), as otherwise some easily oxidisable metals may become oxidised. This is especially necessary when arsenic, lead, bismuth, tin, or zinc are present.

We found that the compounds of nickel, cobalt, iron, zinc, and tin, with phosphoric acid and silicic acid, behave before the blowpipe in a similar manner to the salts of these metals with volatile acids.

DIFFICULTLY REDUCIBLE METALLIC OXIDES.

Iron, Chromium, Aluminium, Cobalt, and Manganese.

Experiments were made with the compounds of the above-mentioned metals, as with the compounds of the

* From the Scientific Proceedings of the Royal Dublin Society.

FIRST SERIES OF EXPERIMENTS.

(Silver Chloride Mixed with the Substance and Fluxes before Fusion).

EASILY REDUCIBLE METALLIC OXIDES.

Metal.	Quantities of Fluxes and substance.	Deci-grms.	Reduction.	Remarks.
1. Antimony	Tartar emetic	3	Practically complete.	Fusion went well, both beads easily fusible. Assay was cooled in stream of coal-gas. A very slight trace of antimony was found in glass bead.
	Bicarbonate of soda..	3		
	Borax.. .. .	12		
	Silver chloride.. ..	12	Incomplete.	Tin in fair quantity was found in both beads. Both beads were easily fusible. In another experiment silica was added, but without beneficial result.
2. Tin	Stannic oxide	3		
	Bicarbonate of soda..	3		
	Borax.. .. .	6	Complete.	Both beads easily fusible. Assay was cooled in coal-gas. On testing glass bead, no lead was found. With lead, the whole assay must be kept covered with a good reducing flame during the entire fusion.
3. Lead	Lead acetate crystals	3		
	Bicarbonate of soda..	3		
	Borax.. .. .	6	Complete.	It will be noted that the proportions used are the same as those usually employed. The actual weights were taken small, as it was feared that the volatilisation of arsenic might be troublesome. This, however, was not found to be the case: the volatilisation was very slight, and was confined to the beginning of the fusion. The fusion went easily; the assay was cooled in coal-gas. No arsenic was found on testing the glass bead, but a large quantity was found in the metallic bead.
4. Arsenic ..	Silver chloride.. ..	12		
	Arsenic trioxide	1		
	Bicarbonate of soda..	1	Complete.	Great difficulty was experienced in getting a fusible metallic bead. The glass bead, on cooling, became in parts white and opaque, and small quantities of metallic scale came up on its surface. On testing the glass bead, no silver was found.
	Borax.. .. .	4		
	Silver chloride.. ..	4		
5. Silver ..	Silver nitrate	3	Complete.	Metallic bead was very easily fusible. On testing the borax bead, no bismuth was found.
	Borax.. .. .	12		
	Bismuth nitrate crystals	1		
6. Bismuth ..	Bicarbonate of soda..	2	Complete.	This fusion was gradually heated. The assay was cooled in coal-gas; the glass bead obtained was clear and transparent. The borax bead was tested for copper, but none was found. Experiments were tried, in which varying quantities of litharge were used instead of silver chloride, but the reduction was in all such cases incomplete.
	Borax.. .. .	6		
	Silver chloride.. ..	8		
7. Copper ..	Copper sulphate crystals	3	Complete.	With these small quantities the fusion went very well, both beads being sufficiently fusible. On testing the borax bead for nickel, none was found present. With larger quantities the results were not satisfactory. Other experiments were made without the use of arsenic, but in all cases the greatest difficulty was experienced in getting a fusible bead, even when the proportion of silver chloride to nickel chloride was 1 to 40. Litharge was tried instead of silver chloride, but though a fusible bead resulted, the fusion was not a success.
	Bicarbonate of soda..	3		
	Borax.. .. .	12		
	Silver chloride.. ..	12	Complete.	Both beads were very easily fusible. The metallic bead tailed like impure mercury, and was more fusible than the glass bead. The amount of arsenic volatilised was inconsiderable. The assay was cooled in coal-gas. On testing, zinc was found in both beads. Other experiments were made without the use of arsenic, but the metallic bead was infusible in all cases except where litharge was employed. In some experiments silica was added to the charge, but without good result.
8. Nickel ..	Nickel chloride	5		
	Borax.. .. .	15		
	Metallic arsenic	15	Incomplete.	
	Silver chloride.. ..	10		
9. Zinc	Zinc sulphate	3	Incomplete.	
	Bicarbonate of soda..	3		
	Borax.. .. .	6		
	Metallic arsenic	15	Incomplete.	
	Silver chloride.. ..	12		

NOTE.—The experiments tabulated above are those which we regard as having given the most satisfactory results in each case.

easily reducible oxides. The results were somewhat surprising. In each case, the silver immediately on reduction, became infusible, or very difficultly fusible, but on heating the reduced silver for a long time, with the tip of a good oxidising flame, it could in all cases be made fusible.

Under the conditions of the experiment, it was thought probable that these metals were, at least to a small extent, reduced. It seemed to us possible that a small quantity might become reduced before the substance could be dissolved in the borax; and if this occurred we should expect the alloy formed to be infusible or difficultly fusible.

To avoid such possible reduction, the substances were first fused with borax alone on charcoal, in the oxidising flame, the glass bead was then powdered, mixed with the silver chloride, and heated in the reducing flame; the results was not more satisfactory, the metallic bead in each case became infusible soon after reduction. It was found that small quantities of iron and cobalt were reduced even when their compounds were heated with borax alone in the oxidising flame, the reduced metal was always found as a thin film or small globules on that surface of the glass which had cooled in contact with the charcoal. In each of these experiments the weight of substance taken was 3 decigrams., and of borax 12 decigrams.

Some experiments were next made with cobalt chloride to ascertain whether by decreasing the weight of salt experimented upon this reduction could be prevented. It was found that even when a mixture of 1 centigram. of cobalt chloride, and 40 centigrams. of borax were fused in the oxidising flame, some cobalt was reduced, though only a very minute quantity.

In the experiments with cobalt, the metallic bead always became very difficultly fusible; and on solidifying it entirely lost its globular form, and flattened out in a very remarkable manner, sometimes even becoming branched. A similar flattening of the metal bead was observed in the case of chromium, and to some extent in that of aluminium.

No experiments were made on manganese in this series.

The number of experiments made with difficultly reducible oxides in this series was very large, but as the results obtained were of a negative character, we have not considered it necessary to give the details of the individual experiments.

(To be continued).

ANALYSIS OF SODIUM ALUMINATE.

By G. LUNGE.

A KNOWN quantity of the sample is dissolved in a given quantity of water, the proportion of residue insoluble in water being determined at the same time. A measured quantity of the solution is mixed with phenolphthalein, and titrated whilst hot with normal acid until the red colour disappears. The result shows the quantity of soda combined with alumina or silica. There is then added to the same liquid one drop of the solution of methyl orange, and it is titrated further. During this second titration the liquid is to be kept moderately warm, say 30°–37°. If necessary it is either cooled or set in a warm place. The titration is completed when the yellow colour of the liquid changes to a permanent red. As now all the alumina is converted into aluminium chloride or sulphate, the alumina present can be simply calculated from this titration. It is at once found in grms. by multiplying the difference of the two readings of the burette by 0.017; if normal acid has been used, or by 0.0017 in case of decinormal acid.

In technical determinations small quantities of silica, if present, may be neglected. It is more accurate to

determine them and deduct their amount calculated as orthosilicate. The presence of large quantities of silica, however, excludes the use of the titration method.—*Zeit. Anal. Chemie*, vol. xxx., p. 471.

NOTICES OF BOOKS.

Examination of Water for Sanitary and Technical Purposes. By HENRY LEFFMANN, M.D., Ph.D., and W. BEAM, M.A. Second Edition, Revised and Enlarged, with Illustrations. Philadelphia: Blakiston, Son, and Co. London: Kegan Paul, Trench, Trübner, and Co. 8vo., pp. 130.

THIS work does not cover exactly the same ground as that by Professor Wanklyn, the eighth edition of which we had the pleasure of noticing a few weeks ago. As regards the strictly chemical examination of waters the two works run nearly parallel. Both give very similar instructions for the collection of samples, though Messrs. Leffmann and Beam use in place of the Winchester quart, commonly employed in Britain, the Penn "Demijohn,"—a kind of case bottle not known in this country. A useful hint is that "care should be taken to fill the vessel with as little agitation with air as possible." The instructions for the determination of total solids and chlorine call for no remark.

For the determination of nitrogen present as ammonia, and in organic compounds, the authors give the well-known Wanklyn process. To colorimeters they give the name "colour comparators." The Frankland and Armstrong method they consider liable to inaccuracies, but they describe and recommend the Kjeldahl process. The determination of the "oxygen consuming" power, as carried out by means of permanganate according to the instructions of Drs. Tidy and Dupré, is fully described, although the authors remark that such methods are limited in value.

Fleck's process (reduction effected by boiling the water with an alkaline solution of silver thiosulphate), they find open to the same objections as the permanganate process without any decided advantage.

They describe a process—the molybdc method—for the detection and determination of soluble phosphate, and they regard the presence of more than 0.6 part per million of PO_4 a suspicious feature, though its absence is no positive proof of freedom from organic pollution. Professor Wanklyn, on the other hand, attaches little importance to the presence of phosphates. Heisch's well-known sugar-test, according to F. E. Lott and Dr. Frankland, develops fungoid growths most decidedly in a water containing soluble phosphates. Our own experience convinces us that in any process for the treatment of sewage and other waste waters, the elimination of such phosphates is a necessary condition of success.

A method for the determination of free oxygen in water is given as proposed by Blarez. Among poisonous metals which may be present in waters the authors do not, like too many authorities, overlook chromium, which in manufacturing districts is far from uncommon. Boric acid, we think, will rarely be present.

For the spectroscopic examination of water, which may sometimes be useful, the authors use a small direct vision spectroscope. They also recommend in some cases a determination of specific gravity. But their method of procedure seems to us less satisfactory than that of Wanklyn, nor do they propose to use it, as he does, as a check on the total results of analysis.

The action of water upon lead is made the subject of a section. The following substances are specified as promoting the corrosion of lead piping: free acids and alkalies, oxygen, nitrates, especially those of potassium and ammonium, chlorides, and sulphates. On the other

hand, the following substances are characterised as non-corrosive and as preventing corrosion: calcium carbonates, acid sodium and ammonium, calcium silicate, silica, and soluble phosphates.

The degree of hardness has, in the opinion of the authors, little bearing on its sanitary value. This may be true as regards water ingested, though accurate comparative experiments are still wanting. But it cannot be accepted where the use of the waters for personal ablution is concerned. To wash in hard waters with the aid of soap is well known to coat the skin with a gluey film which cannot other than interfere with the free action of the pores.

Instructions for the biological examination of water are given at some length. The remark is made that "the presence of any of the higher orders of organic forms may be taken as an indication of moderate purity, as these are absent from very foul water." This rule cannot be absolutely accepted, since certain plants, *e.g.*, water-cress, flourish better in undiluted sewage than in river water. But in industrial waste waters the higher animals and plants will certainly be absent. *Beggiatoa alba* indicates sulphur compounds rather than organic pollution. In concluding this chapter the authors admit that bacteriological studies, though often difficult to interpret, have yet been in certain cases of much value.

In speaking of the technical applications of water, magnesium chloride is justly pronounced very hurtful. The examination of a water for steam purposes should, it is said, include determination of free acid, total solids, SO_4 , Cl, Ca, Mg, temporary and permanent hardness. No general rules are laid down for general manufacturing purposes, save that the nearest possible approach to chemical purity should be sought for. The dangers attending the presence of iron in the waters used in dye and bleach works are not overlooked.

The book before us may be safely recommended for the use of sanitary officials, analysts, and industrial analytical chemists as a useful addendum to their reference-works.

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY AND ADVERTISING CERTIFICATES.

To the Editor of the Chemical News.

SIR,—The communication of Dr. Arthur P. Luff in your last number (*CHEM. NEWS*, vol. lxi., p. 176) raises many important issues, which require consideration not merely from a purely ethical standpoint, but also with regard to the commercial interests of those parties who advertise analytical certificates.

That the Institute of Chemistry could and should pursue some course of action, besides existing, collecting fees, and issuing a periodical register, is the opinion of certainly a majority of its members. Just as Macaulay said there are in a Turkey carpet all the colours which, when properly arranged, will make a picture, so it may be said there are in the Institute of Chemistry all the elements necessary to the constitution of an ideal professional Institute; but there is, unfortunately, a considerable lack of arrangement. Perhaps when other chemical interests than those of the professorial class are more adequately represented on the governing body, a healthful desire to be more useful may be witnessed in that quarter. Whatever might be done, however, it would be of the greatest importance to take care that while a judicious control should certainly be exercisable, as Dr. Luff suggests, over palpably dishonest or professionally immoral conduct, there should be no undue interference with the liberty of the subject. Commercial men and firms have a perfect right to seek testimony to the value of their

products and processes from a particular or a general point of view; and they also have an indefeasible right to use the testimony for which they pay. Of what earthly use is it to a manufacturer in these days to have a good article and to have it so certified unless he be allowed to publish such evidence?

There is a good deal of sentiment current amongst many medical men as to the publication of their views concerning things commercial; but perhaps this is only reasonable, since medical opinions are not, in the great majority of instances, based upon ascertained facts: they are sometimes built up upon a basis of experience, but cannot be put to any real test, or they are mere expressions of personal conviction not infrequently of a worthless character.

I do not desire for one moment to defend any really dishonest or otherwise blameworthy conduct of analytical and consulting chemists, but so long as their reports deal with matters of fact, and the inferences fairly deducible from them, they should be allowed full liberty of action.

Writing as a manufacturer and as a professional chemist, it seems to me that if manufacturers are not to be allowed to publish as they please proper reports for which they are willing to pay, they will certainly not engage the services of gentlemen who are so finikin concerning the discharge of one of the most important functions of their professional life, *viz.*, certifying to the manufacturer and to the public alike, certain definite values of commodities, &c., offered for public sale or use; but the manufacturer will get the evidence he requires all the same, to the loss only of the said professional men.

I offer these remarks not so much by way of reply to Dr. Luff, whose views may or may not coincide with mine, but because I think if the subject is to be discussed it cannot be thrashed out too exhaustively.—I am, &c.,

C. T. KINGZETT, F.I.C., F.C.S.

ESTIMATION OF NITRIC ACID.

To the Editor of the Chemical News.

SIR,—In nearly all works on Analysis, the method of estimating nitric acid by means of the "copper zinc couple" is given. I have tried the plan as given in Thorpe's "Quantitative Analysis," but always with a perfectly negative result. A pupil of mine who has made several attempts recently has arrived at the same result. Is there any special procedure to be adopted?

I have obtained very satisfactory results by the following process:—About half a gm. of KNO_3 is boiled with the "couple," an excess of oxalic acid being added. The boiling is continued for half an hour, then soda added, and the distillation carried on as usual for the estimation of ammonia.

I may mention that I have always succeeded by digesting a nitrate with the "couple" for some time in an acid solution and then "nesslerising" the solution.—I am, &c.,

W. A. RUDGE.

Devon Lodge, Plymouth.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 12, September 21, 1891.

This issue contains no chemical matter.

Moniteur Scientifique, Queneville.
Series 4, Vol. iv., Part 2, No. 587.

New Method for Preparing Chlorine.—P. de Wilde and A. Reyckler.—The authors melt together hydrated magnesium sulphate, 246 parts; magnesium chloride, 203 parts; and manganese chloride, 198 parts. On evaporating away the water of crystallisation, hydrochloric acid escapes and there is obtained a greyish rose coloured residue, hard, brittle, and very hygroscopic, consisting of a mixture of manganese sulphate and chloride, and manganese chloride almost entirely free from water. If this matter is heated to dull redness in contact with air in a muffle, there escape simultaneously hydrochloric acid and chlorine, and there remains a black porous consistent residue, an intimate mixture of anhydrous magnesium sulphate and magnesium manganite, $Mg_3Mn_2O_8$. If this mixture is introduced into a porcelain tube heated to about 425° , there occurs a very regular escape of chlorine mixed with watery vapour, and, towards the end of the operation, a gradually increasing quantity of hydrochloric acid not utilised. One-fourth of the chlorine contained in the hydrochloric acid escapes in the shape of gaseous concentrated chlorine, and the remaining three-fourths are transformed into anhydrous magnesium and manganese chlorides. The tube is then raised to 525° and is traversed by a current of dry air, when there occurs a new escape of chlorine. The mixture of magnesium sulphate and magnesium manganite is then re-constituted and can again be submitted to the action of hydrochloric acid below nascent redness, which is anew followed by treatment with air at nascent redness, and so continuously. The authors allege that by their process the minimum yield is 70 per cent of the hydrochloric acid employed, whilst Weldon's process yields only 30 per cent. It appears that in France the price of hydrochloric acid (strength ?) has risen from 6 to 7 francs per 100 kilos.

New Method for the Volumetric Analysis of Sulphur Chloride.—G. A. Le Roy.—The author's method is based on the use of standard solutions. The chloride of sulphur is weighed into a tared phial and measured with a pipette of narrow calibre. The quantity is received into a dilute solution of pure soda ($10.37 \text{ Na}_2\text{O}$ per litre = 10 grms. sulphur per litre), of which a known volume has been taken. The chloride is decomposed, yielding sodium sulphide, thiosulphate, sulphite, sulphate, and chloride, and free sulphur separates out. It is heated, when the free sulphur quickly dissolves. When all the sulphur has disappeared, pure oxygenated water is added to the refrigerated liquid, which is then gently heated. The compounds of sulphur combined with soda are thus oxidised and converted into sodium sulphate. The excess of oxygenated water is then destroyed by heating the liquid to ebullition. The residual excess of soda is then titrated with a standard solution of pure nitric acid ($39.35 \text{ NO}_3\text{H}$ per litre), in presence of litmus or orange 3 as indicator. To this quantity of soda thus determined there is added the quantity of soda corresponding to the sodium contained in the sodium chloride formed by the action of the sulphur chloride, a quantity determined in the second part of the process (determination of chlorine). This total is deducted from the quantity of soda originally used; the difference represents the quantity of soda transformed into sodium sulphate, from which the sulphur is calculated. $n \text{ c.c. of the solution of soda sulphated } \times 0.010 = N \text{ grms. of sulphur}$. In the liquid, neutralised, and thus freed from sulphides or thiosulphates, we determine the chlorine by a standard solution of silver in the known manner.

Vegetable Butter.—F. Jean.—An alimentary fat has for some time been manufactured at Mannheim from the oils of the kernel of the cocoanut (*Cocos nucifera*). A hectare of cocoa palms, representing 225 trees, yields yearly 800 kilos. of oil. Hitherto the use of these oils has been hindered by their acrid flavour; but by treatment with alcohol and animal charcoal the rancid flavour is

removed, and the product is rendered white. This purified fat is now manufactured at Argenteuil and Amsterdam. It is the only fat which is analogous to cow butter, as it contains the same proportion of soluble fats. It has the advantage of being perfectly free from pathogenic organisms. (Could not this cocoanut butter be made more economically in India, Ceylon, &c., thus dispensing with the carriage of the useless parts of the nut ?)

Syntheses effected in the Group of the Sugars.—Emile Fischer.—A lecture delivered before the German Chemical Society.

On Bees'-Wax.—A. and P. Buisine.—The completion of a long illustrated paper.

On Bleaching - Chlorides.—MM. Osterberger and Capelle.—An exposure of certain alleged substitutes for bleaching-lime.

Preparation of certain Fluorides, and their Industrial Value.—Max Metto (*Zeit. Ang. Chemie*).—Process for obtaining artificial cryolites.

Process for Preparing Aluminium Hydroxide and the Alkaline Aluminates.—(*Dingler's Journal*).—The alkaline liquor resulting from the decomposition of the aluminate is concentrated by evaporation and then calcined directly with beauxite.

Presence of Vanadium in Caustic Potassa.—Edgar Smith.—From the *CHEMICAL NEWS*.

Preparation of Crystalline Iron Disulphide from Anhydrous Ferric Chloride and Phosphorus Pentasulphide.—E. Glatzel.—From the *Berichte d. Deut. Chem. Gesellschaft*.

Coefficient of the Utilisation of Gases.—C. W. Jurisch (*Chemische Industrie*).—A purely mathematical paper.

On Wool.—Dr. A. Horwitz (*Faerber Zeitung*).—This memoir seems founded on a lecture delivered by Prof. Watson Smith, F.C.S., before the Society of Dyers and Colourists. The author remarks that without its normal lustre wool has the appearance of cotton, and if the lustre exceeds a certain degree the wool is more transparent and does not take all colours equally well. Hence, if it is mixed with normal wool it may occasion uneven shades. In dyed wools, the hygroscopic property varies with the colour. The absorption of moisture decreases in the following series:—Black, blue, red, green, yellow, and white.

The Constituent Principles of Linen.—C. F. Cross and E. J. Bevan.—From the *Journal of the Chemical Society*.

Distinction of the Fibres of Jute, Linen, and Hemp.—W. Lenz.—Already noticed under *Zeitschrift Anal. Chemis.*

New Methods of Preparing Waterproof Cloth.—Em. Döring (*Romen's Journal*).—These methods may be divided into two groups. In some, a precipitate of salts of the fatty acids is produced upon the tissue itself; in others, the cloth is saturated with melted or dissolved substances, which, when they are once solidified on the fibre, have the property of repelling water. If any of the former class of methods is selected, the cloth is passed into a special machine in which it is saturated with aluminium acetate; it is dried and passed into a soap-beck. It is necessary in this operation to produce a basic compound. For this purpose, there are employed equal weights of salts of aluminium and of lead. Care must be taken not to introduce too large quantities of free acid with the aluminium sulphate, since the latter contains always a certain quantity of sulphuric acid, which, during desiccation, displaces the acetic acid. To avoid this inconvenience, there are added per litre from 10–80 grms. of soda. The most favourable temperature is 50° . Heating by direct steam must be avoided. For preparing the soap bath the author utilises the fact that an aqueous solution of soap forms true solutions with

mixtures of fat and wax, resins, mineral oils, and even caoutchouc. To this end, he takes a 10 per cent solution of gum paraguay in oil of turpentine. The proportions to be employed for a square metre of cloth are 30 grms. tallow soap, 25 Japan wax, 1.5 gum paraguay, 1 gm. good varnish. The wax is first melted, the gum and the varnish are added, and then for each kilo. of the solid gum there are added 0.5 gm. of a solution, saturated in heat, of potassium sulphide (liver of sulphur). The mixture is stirred and boiled, when sulphuretted hydrogen is liberated. A boiling solution of soap is added, when the bath is fit for use.

Sugars, Starches, and Gums.—Papers from the *Chemiker Zeitung*, *Liebig's Annalen*, the *American Chemical Journal*, and the *Zeit. Anal. Chem.*

Identity of Cerebrose and Galactose.—H. Brown and Harris Morris.—From the *Journal of the Chemical Society*.

On Arabinose.—C. O'Sullivan.—From the *Journal of the Chemical Society*.

Detection of Nitrous Products in Sulphuric Acid.—H. Wilson.—From the *Pharmaceutical Journal*.

Determination of Nitrous Acid in Presence of Nitric Acid.—W. Kalmann.—From the *Zeit. Anal. Chem.*

The Double Potassium and Mercury Iodide as a Reagent for Aldehyds.—L. Grismer (*Deutsch. Chemiker Zeitung*).—The aldehyds give with an alkaline solution of double potassium and mercury iodides a precipitate which varies from yellowish white to reddish brown or black, according to the dilution.

Detection of Traces of Copper in Distilled Water.—Herman Thoms (*Pharm. Central Halle*).—Distilled water, the purity of which has been ascertained by the ordinary methods, becomes coloured yellow on dissolving in it potassium iodide. A closer examination admits of the detection of infinitesimal quantities of copper, which neither ammonia nor potassium ferrocyanide had revealed. The presence of this impurity occasions the yellow colouration of the solution of potassium iodide in the water. The reagent gives a feeble yellow colouration with 1 part in 200,000 parts of water. The liquid must not contain any other substance capable of decomposing the iodide and liberating iodine.

MISCELLANEOUS.

Sulphuric Anhydride.—In the Chemical Section of the recent Congress of German Naturalists and Physicians, Prof. Dr. Rud. Weber exhibited a series of preparations from the Plettenberg Works in Westphalia, which are sent out in soldered tin boxes containing 2½ kilos. each. The anhydride was made according to Winkler's method, but no details were given. The speaker discussed the view as to the existence of two allotropic forms of sulphuric anhydride. According to his (Weber's) careful investigations, in which the anhydride was obtained absolutely free from moisture, by treatment with P_2O_5 and repeated distillation, it is in this state, at temperatures above 15° , a liquid which on cooling congeals to crystals resembling saltpetre, but which melt at the heat of the hand. Very small proportions of water cause this liquid to congeal at the heat of common temperatures, and the solid thus formed does not melt below 100° . It is a new compound, which in its empirical composition corresponds to the formula $4SO_3 + H_2O$. Sulphuric anhydride enters into direct combination with sulphur, selenium, and tellurium. With the former it yields a blue compound, insoluble in an excess of the anhydride, which Weber calls sulphur sesquioxide, S_2O_3 . Selenium dissolves in the anhydride to a deep green compound, $SeSO_3$, and tellurium to a red liquid, $TeSO_3$.—*Chemiker Zeitung*.

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THE CHEMICAL NEWS.

VOL. LXIV., No. 1664.

THE ORIGIN OF PETROLEUM.*

By O. C. D. ROSS, M.Inst.C.E.

PETROLEUM is one of the most widely distributed substances in Nature, but the question how it was originally produced has never yet been satisfactorily determined, and continues a problem for philosophers. In 1889 the total production exceeded 2,600,000,000 gallons, or about 10,000,000 tons, and, at fourpence per gallon, was worth about £44,000,000, while the recognition of its superior utility as an economical source of light, heat, and power, steadily increases; but, notwithstanding its importance in industry, the increasing abundance of the foreign supply, and the ever widening area of production, practical men in England continue to distrust its permanence; and owing to the mystery surrounding its origin, and the paucity of indications where and how to undertake the boring of wells, they hesitate to seek for it in this country, or even to extend the use of it whenever that would involve alterations of existing machinery. The object of this paper is to suggest an explanation of the mystery which seems calculated to dissipate that distrust, since it points to very abundant stores, both native and foreign, yet undiscovered, and even in some localities to daily renovated provisions of this remarkable oil.

The theories of its origin suggested by Reichenbach, Berthelot, Mendeleeff, Peckham, and others, made no attempt to account for the exceeding variety in its chemical composition, in its specific gravity, its boiling-points, &c., and are all founded on some hypothetical process which differs from any with which we are acquainted; but modern geologists are agreed that, as a rule, the records of the earth's history should be read in accordance with those laws of Nature which continue in force at the present day, *e.g.*, the decomposition of fish and cetaceous animals could not now produce oil containing paraffin. Hence we can hardly believe it was possible thousands or millions of years ago, if it can be proved, that any of the processes of Nature with which we are familiar is calculated to produce it.

The chief characteristics of petroleum strata are enumerated as:—

- I. The existence of adjoining beds of limestone, gypsum, &c.
- II. The evidence of volcanic action in close proximity to them.
- III. The presence of salt water in the wells.

I. All writers have noticed the presence of limestone close to petroleum fields in the United States and Canada, in the Caucasus, in Burmah, &c., but they have been most impressed by its being "fossiliferous," or shell limestone, and have drawn the erroneous inference that the animal matter once contained in those shells originated petroleum; but no fish oil ever contained paraffin. On the other hand, the fossil shells are carbonate of lime, and, as such, capable of producing petroleum under conditions such as many limestone beds have been subjected to in all ages of the earth's history. All limestone rocks were formed under water, and are mainly composed of calcareous shells, corals, encrinurites, and foraminifera—the latter similar to the foraminifera of "Atlantic ooze" and of English chalk beds. Everywhere, under the microscope, the original connection of limestone with organic matter—its organic parentage, so to speak, and cousin-

ship with the animal and vegetable kingdoms—is conspicuous. When pure it contains 12 per cent of carbon.

Now petroleum consists largely of carbon, its average composition being 85 per cent of carbon and 15 per cent of hydrogen, and in the limestone rocks of the United Kingdom alone there is a far larger accumulation of carbon than in all the coal measures the world contains. A range of limestone rock 100 miles in length by 10 miles in width, and 1000 yards in depth would contain 743,000 million tons of carbon, or sufficient to provide carbon for 875,000 million tons of petroleum. Deposits of oil bearing shale have also limestone close at hand; *e.g.*, coral rag underlies Kimmeridge clay, as it also underlies the famous black-shale in Kentucky, which is extraordinarily rich in oil.

II. As evidence of volcanic action in close proximity to petroleum strata, the mud volcanoes at Baku and in Burmah are described, and a sulphur mine in Spain is mentioned (with which the writer is well acquainted), situated near an extinct volcano, where a perpetual gas-flame in a neighbouring chapel and other symptoms indicate that petroleum is not far off. While engaged in studying the geological conditions of this mine, the author observed that Dr. Christoff Bischoff records in his writings that he had produced sulphur in his own laboratory by passing hot volcanic gases through chalk, which, when expressed in a chemical formula, leads at once to the postulate that, in addition to sulphur, *ethylene* and all its homologues (C_nH_{2n}), which are the oils predominating at Baku, would be produced by treating—

2, 3, 4, 5 equivs. of carbonate of lime (limestone) with
2, 3, 4, 5 " sulphurous acid (SO_2) and
4, 6, 8, 10 " sulphuretted hydrogen (H_2S);

and that marsh-gas and its homologues, which are the oils predominating in Pennsylvania, would be produced by treating—

1, 2, 3, 4, 5 equivs. of carbonate of lime with
1, 2, 3, 4, 5 " sulphurous acid and
3, 5, 7, 9, 11 " sulphuretted hydrogen;

Thus we find that—

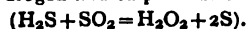
Carbonate of lime, $2CaCO_3$,
Sulphurous acid, $2SO_2$, and
Sulphuretted hydrogen, $4H_2S$, } yield $\left\{ \begin{array}{l} 2(CaSO_4 \cdot H_2O) \\ \text{(gypsum),} \\ 4S \text{ (sulphur), and} \\ C_2H_4, \text{ which is} \\ \text{ethylene.} \end{array} \right.$

And that—

Carbonate of lime, $CaCO_3$,
Sulphurous acid, SO_2 , and
Sulphuretted hydrogen, $3H_2S$, } yield $\left\{ \begin{array}{l} CaSO_4 \cdot H_2O \text{ (gyp-} \\ \text{sum),} \\ 3S \text{ (sulphur), and} \\ CH_4, \text{ which is} \\ \text{marsh-gas,} \end{array} \right.$

So that these and all their homologues, in fact petroleum in all its varieties, would be produced in Nature by the action of volcanic gases on limestone.

But much the most abundant of the volcanic gases appear at the surface as steam, and petroleum seems to have been more usually produced without sulphurous acid, and with part of the sulphuretted hydrogen (H_2S) replaced by H_2O (steam) or H_2O_2 (peroxide of hydrogen), which is the product that results from the combination of sulphuretted hydrogen and sulphurous acid—



It is a powerful oxidising agent, and it converts sulphurous into sulphuric acid. Thus—

$CaCO_3$,
 H_2S ,
 $2H_2O$, } yield $\left\{ \begin{array}{l} CaSO_4 \cdot H_2O \text{ (gypsum)} \\ \text{and} \\ CH_4, \text{ which is marsh-gas.} \end{array} \right.$

And—

$2CaCO_3$,
 $2H_2S$,
 $2H_2O_2$, } yield $\left\{ \begin{array}{l} 2CaSO_4 \cdot H_2O \\ \text{and} \\ C_2H_4, \text{ which is ethylene.} \end{array} \right.$

Tables are given at the end of the paper showing the formulæ for the homologues of ethylene and marsh-gas

* Abstract of a Paper read before the British Association, Cardiff Meeting, 1891, Section G.

Formulae Showing how Ethylene and its Homologues (C_nH_{2n}) are Produced by the Action of the Volcanic Gases H₂S and H₂O₂ on Limestone.

Carbonate of lime.		Sulphuretted hydrogen.		Peroxide of hydrogen.	yield	Gypsum.		Ethylene and its homologues.	
2CaCO ₃	+	2H ₂ S	+	2H ₂ O ₂		2(CaSO ₄ .H ₂ O)	+	C ₂ H ₄ ethylene (gaseous).	
3CaCO ₃	+	3H ₂ S	+	3H ₂ O ₂	"	3(CaSO ₄ .H ₂ O)	+	C ₃ H ₆	
4CaCO ₃	+	4H ₂ S	+	4H ₂ O ₂	"	4(CaSO ₄ .H ₂ O)	+	C ₄ H ₈	
5CaCO ₃	+	5H ₂ S	+	5H ₂ O ₂	"	5(CaSO ₄ .H ₂ O)	+	C ₅ H ₁₀	
6CaCO ₃	+	6H ₂ S	+	6H ₂ O ₂	"	6(CaSO ₄ .H ₂ O)	+	C ₆ H ₁₂	
7CaCO ₃	+	7H ₂ S	+	7H ₂ O ₂	"	7(CaSO ₄ .H ₂ O)	+	C ₇ H ₁₄	Boiling-point.
8CaCO ₃	+	8H ₂ S	+	8H ₂ O ₂	"	8(CaSO ₄ .H ₂ O)	+	C ₈ H ₁₆	189° C.
9CaCO ₃	+	9H ₂ S	+	9H ₂ O ₂	"	9(CaSO ₄ .H ₂ O)	+	C ₉ H ₁₈	136° C.
10CaCO ₃	+	10H ₂ S	+	10H ₂ O ₂	"	10(CaSO ₄ .H ₂ O)	+	C ₁₀ H ₂₀	160° C.
11CaCO ₃	+	11H ₂ S	+	11H ₂ O ₂	"	11(CaSO ₄ .H ₂ O)	+	C ₁₁ H ₂₂	180° C.
12CaCO ₃	+	12H ₂ S	+	12H ₂ O ₂	"	12(CaSO ₄ .H ₂ O)	+	C ₁₂ H ₂₄	196° C.
13CaCO ₃	+	13H ₂ S	+	13H ₂ O ₂	"	13(CaSO ₄ .H ₂ O)	+	C ₁₃ H ₂₆	240° C.
14CaCO ₃	+	14H ₂ S	+	14H ₂ O ₂	"	14(CaSO ₄ .H ₂ O)	+	C ₁₄ H ₂₈	247° C.
15CaCO ₃	+	15H ₂ S	+	15H ₂ O ₂	"	15(CaSO ₄ .H ₂ O)	+	C ₁₅ H ₃₀	—

resulting from the increase in regular gradation of the same constituents.

It is explained that these effects must have occurred, not at periods of acute volcanic eruptions, but in conditions which may be, and have been observed at the present time, wherever there are active solfataras or mud volcanoes at work. Descriptions of the action of solfataras by the late Sir Richard Burton and by a British Consul in Iceland are quoted, and also a paragraph from Lyall's "Principles of Geology," in which he remarks of the mud volcanoes at Girgenti (Sicily) that *carburetted hydrogen* is discharged from them, sometimes with great violence, and that they are known to have been casting out water, mixed with mud and *bitumen*, with the same activity as now for the last fifteen centuries. Probably at all these solfataras, if the gases traverse limestone, fresh deposits of oil-bearing strata are accumulating, and the same volcanic action has been occurring during many successive geological periods and millions of years; so that it is difficult to conceive limits to the magnitude of the stores of petroleum which may be awaiting discovery in the subterranean depths.*

Gypsum may also be an indication of oil bearing strata for the substitution in limestone of sulphuric, for carbonic acid can only be accounted for by the action of these hot sulphurous gases. Gypsum is found extensively in the petroleum districts of the United States, and it underlies the rock-salt beds at Middlesboro', where, on being pierced, it has given passage to oil-gas, which issues abundantly, mixed with brine, from a great depth.

III. Besides the space occupied by "natural gas," which is very extensive, 17,000 million gallons of petroleum have been raised in America since 1860, and that quantity must have occupied more than 100,000,000 cubic yards, a space equal to a subterranean cavern 100 yards wide by 20 feet deep, and 82 miles in length, and it is suggested that beds of "porous sandstone" could hardly have contained so much; while vast receptacles may exist, carved by volcanic water out of former beds of rock salt adjoining the limestone, which would account for the bine that usually accompanies petroleum. It is further suggested that when no such vacant spaces were available, the hydrocarbon vapours would be absorbed into, and condensed in, contiguous clays and shales, and perhaps also in beds of coal, only partially consolidated at the time.

There is an extensive bituminous limestone formation in Persia, containing 20 per cent of bitumen, and the

* Professor J. Le Conte, when presiding recently at the International Geological Congress at Washington, mentioned that in the United States extensive lava floods have been observed covering areas from 10,000 to 100,000 square miles in extent, and from 2000 to 4000 feet deep. We have similar lava flows and ashes in the North of England, in Scotland, and in Ireland, varying from 3000 to 6000 feet in depth. In the Lake District they are nearly 12,000 feet deep. Solfataras are active during the intermediate, or so-called "dormant," periods which occur between acute volcanic eruptions

theory elaborated in the paper would account for bitumen and oil having been found in Canada and Tennessee embedded in limestone, which fact is cited by Mr. Peckham as favouring his belief that some petroleum are a "product of the decomposition of animal remains."

Above all, this theory accounts for the many varieties in the chemical composition of paraffin oils in accordance with ordinary operations of Nature during successive geological periods.

ON A COMBINATION OF WET AND DRY METHODS IN CHEMICAL ANALYSIS.*

PART I.

By W. E. ADENEY, F.I.C., Assoc. R.C.Sc.I., Curator, Royal University of Ireland; and T. A. SHEGOG, A.I.C., Assoc. R.C.Sc.I., Assist. Chemist, Royal College of Science, Dublin.
(Concluded from p. 187.)

SECOND SERIES OF EXPERIMENTS.

ANOTHER series of experiments was now made differing from the preceding ones in this respect. In all cases the substance and fluxes were fused together in a shallow cavity in charcoal, the oxidising flame being employed, the beads on cooling were transferred to a cavity of the usual shape and size, metallic silver added in the form of a button, and the whole heated in the reducing flame.

Difficultly Reducible Metallic Oxides.

Three decigrams of each substance, fused with twelve decigrams of borax in the oxidising flame on charcoal, then nine decigrams. (in the case of cobalt, twelve decigrams.) of silver in the form of a button added, and the fusion continued, the reducing flame being employed.

Iron (Ferrous Sulphate).—The metallic bead became quite infusible, but fused when the flame was removed; a very faint trace of iron was found in the metallic bead.

Cobalt (Cobalt Chloride).—The metallic bead was difficultly fusible on cooling; it flattened out in the way already described for cobalt (see First Series of Experiments). It was found on testing to contain a small quantity of cobalt.

Aluminium (Aluminium Phosphate).—The metallic bead was somewhat infusible. Throughout the fusion a considerable quantity of metallic scale appeared on the glass bead. On testing the metallic bead, aluminium was found present.

Chromium (Chromium Nitrate).—The metallic bead was very difficultly fusible; on solidifying, it flattened out as already described for cobalt and chromium (see First Series of Experiments). On testing, a small quantity of chromium was found present.

* From the Scientific Proceedings of the Royal Dublin Society.

Easily Reducible Metallic Oxides.

Metal.	Quantities of Fluxes and substance.	Deci-grms.	Reduction.	Remarks.
Antimony ..	Tartar emetic	3	Practically complete.	The fusion requires great care, and must be cooled in coal-gas. A very minute trace of antimony was found in the borax bead.
	Borax.. ..	12		
	Silver.. ..	9		
Tin	Stannic oxide	3	Incomplete.	The fusion went well, though the metallic bead was somewhat difficult to fuse. The assay was cooled in coal-gas. Although every care was taken, it was found impossible to entirely reduce the tin. The glass bead was quite transparent. An experiment was made, using the same quantities of stannic oxide and borax; but, instead of silver, 12 decigrams. of metallic lead were added. This was unsuccessful, as the tin showed little tendency to alloy with the lead.
	Borax.. ..	12		
	Silver.. ..	9		
Lead	Lead acetate	3	Complete.	The fusion went very well, but was found to require great care. It was cooled in coal-gas. The borax bead was found to contain a trace of lead, but so small as to be inappreciable.
	Borax.. ..	12		
	Silver.. ..	12		
Arsenic . . .	Arsenic trioxide ..	3	Complete.	Volatilisation of arsenic occurred at the beginning of the fusion, but soon ceased. The fusion went easily, and a perfectly transparent glass bead was obtained. The assay was cooled in coal-gas. The glass bead was found to contain a scarcely detectable quantity of arsenic.
	Borax.. ..	12		
	Silver.. ..	9		
Silver	Borax.. ..	12	Incomplete.	The silver remained easily fusible.
	Silver.. ..	9		
	Bismuth nitrate crystals.. ..	3		
Bismuth ..	Borax.. ..	12	Incomplete.	The fusion went very satisfactorily. It was cooled in coal-gas. A small quantity of bismuth was found on testing the glass bead.
	Silver.. ..	12		
	Copper sulphate (anhydrous)	3		
Copper.. ..	Borax.. ..	12	Complete.	The fusion requires care. The borax bead was of a pale bottle-green colour (proved to be due to iron). On testing the glass bead with sulphuretted hydrogen a very slight colouration was observed.
	Silver.. ..	9		
	Nickel chloride ..	3		
Nickel, No. 1	Borax.. ..	12	Practically complete.	The fusion went fairly well, no fumes of arsenic were seen, and its volatilisation could only be detected by the garlic odour observed. The metallic bead was somewhat infusible, remaining all the time in a viscous state. The glass bead was tested for arsenic and nickel, and a mere trace of each was found present.
	Sodium arsenate ..	2		
	Silver.. ..	4		
No. 2	Nickel chloride ..	5	Practically complete.	The fusion went well, both beads were easily fusible. The borax bead contained a mere trace of nickel.
	Borax.. ..	25		
	Silver.. ..	33		

NOTE.—No experiments were made with zinc in this series.

Manganese (Manganous Sulphate).—The metallic bead was at first infusible, but became more fusible towards the end of the experiment. A good deal of metallic scale appeared floating on the glass bead, even before the silver was added. On testing the metallic bead, manganese was found present.

It now only remains for us to make a brief reference to what has been done towards the solution of the third of the questions we wished to settle, namely, whether or not, when complex substances are fused with borax and sodium carbonate in the manner described, the constituent metals behave as in simple compounds.

In Dr. Davoren's estimations of nickel and cobalt by this method, no difficulty was experienced in effecting a complete separation; the nickel was entirely reduced, and all the cobalt was found in the glass bead. From this it was thought that the presence of an easily reducible oxide might entirely prevent the reduction of a difficultly reducible oxide. It seemed probable that if this were found to be the case with bodies so allied in chemical properties as nickel and cobalt, it would in all probability be true of the other oxides; experiments were therefore made with salts of these metals.

The salts were mixed with borax, and fused in the oxidising flame; no silver was used. The side of the glass bead which had cooled in contact with the charcoal was invariably found covered with a layer of reduced metal. When the proportions of nickel to cobalt in the mixture was greater than 1 to 1, the reduced metal was entirely nickel. When, however, the cobalt preponderated in the mixture, a small quantity was always reduced with the nickel.

It will be seen that a considerable number of experiments are yet required, more especially to ascertain the behaviour of complex substances when treated in the way suggested by us; and it was our original intention to complete the necessary experiments before publishing any results of our investigation. In the midst of our work, however, one of us, having been elected to the office of Curator in the Royal University, had to resign his position in the Royal College of Science. We have since found it impossible to continue the work jointly, and we have therefore thought it advisable to publish an account of the work which has been already done.

The investigation will be carried on by one of us.

A NEW GLASS SYPHONING EXTRACTION APPARATUS.*

By J. T. WILLARD and G. H. FAILYER.

BEFORE describing our apparatus, a few words in justification of its invention, notwithstanding the many forms already proposed, may not be out of place. First, we are led to reject any extractor which makes cork connections. The extreme difficulty of completely freeing cork from its resinous constituents can be appreciated only by one who has extracted the properly perforated corks for one hundred hours or more in a large Soxhlet's extractor, and at the end of that time has still found appreciable quantities of extract. Then, too, the more perfectly a cork is exhausted, the less suited does it become, mechanically, for use, losing its toughness and elasticity. Second, a syphoning apparatus must be preferable to a percolating, because we are certain that every particle of the substance is soaked by fresh solvent every time the container is filled, while in a percolating apparatus we can never be quite sure that the solvent is not chiefly flowing down channels of least resistance and leaving portions of the material comparatively unacted upon. Soxhlet's extractor, when made with ground joints will doubtless give good satisfaction. The form we are about to describe has, however, the advantage of greater simplicity, and is consequently cheaper and less liable to fracture.

By reference to the cut it will be seen that our extractor consists of four parts, viz., the flask, A; the containing tube, B; the condensing tube, D; and the syphon, C. The flask is small, holding about 100 c.c., and weighing about 20 grms. The containing tube is ground into the neck of the flask, and has a pocket on one side, in which the substance, enclosed in a sack formed of fat-free filter-paper, is placed for extraction, and into which the short arm of the syphon dips. The condensing tube expands to a stopper for the containing tube, and at the lower end is drawn out and ground off in such a way as to direct the condensed solvent into the pocket containing the substance for analysis. The upper part of the condensing tube passes through a cold water jacket of some kind; ours is a copper tank large enough for six extractors. The syphon is made of small tubing, the inside diameter being about 2 m.m. At the bend it must be less, but must not be constricted so much as to greatly impede the flow of the liquid through. The capillary attraction exercised by the inner wall of the syphon raises the liquid sufficiently to bring the syphon into action before the pocket is full enough to run over. The upper end of the short limb of the syphon must not be too close to the side of the pocket or the capillary action of the outside of the syphon, and the side of the pocket will draw the liquid over without filling the syphon. To prevent this, the syphon may be bent sharply away from the wall of the pocket, as shown in the cut, or the wall itself may bend away at that point. If the details be met in the construction of the syphon, it will empty the pocket promptly, and the apparatus will require no attention after the flame is adjusted under the water-bath.

The apparatus is so constructed that the syphon may be easily removed, and when the extraction is concluded the substance and the syphon are removed, and the solvent distilled up into the pocket. If too large an excess has not been taken, the removal of the syphon and the substance will give ample capacity to the pocket to

receive the solvent remaining. The drying of the extract is completed in hydrogen as usual.

The extractor, as figured, was constructed for the quantitative analysis of feeding stuffs. The containing pocket was therefore made small to insure quick syphoning and to require but little absolute ether. It is, however, apparent that within certain limits the apparatus might be made of considerable size. We have more recently had a number constructed, especially for milk analysis. In these the containing pocket is made large enough to admit the paper coil upon which the milk is dried if Adams's method is employed, or a drying tube filled with asbestos when desiccation is effected upon that substance. These extractors are each provided with two flasks, thus doubling their efficiency and enabling one to keep them all in constant service.

Our extractors are so arranged that each set of six is heated by a single water-bath. This consists of a flat copper box. The extractors are held up in place by strong spiral brass springs. Each spring has a piece of brass gauze soldered across the upper coil. The diameter of the coil is greater than that of the bottom of the flask. The springs, while rather stiff, must be so adjusted in length as to require but little compression to bring them in position.

We have used the extraction apparatus above described in the analysis of feeding stuffs for over a year and a half with the greatest satisfaction. Fitted with two flasks, and charged with absolute ether, which is protected by a calcium chloride tube in the upper end of the condensing tube, the apparatus seems to us to leave little to be desired in simplicity or perfection of action.

NOTE.—Mr. J. T. Crawley, in the *Am. Chem. Journ.*, vol. xi., p. 507, has described an apparatus employing capillary attraction to bring the syphon into action. It seems right to say that our extractor was designed before the publication of his article.

THE DIRECT DETERMINATION OF ALUMINIUM IN IRON AND STEEL.*

By THOMAS M. DROWN and ALEX. G. McKENNA,
Mass. Institute of Technology, Boston, Mass.

THE unsatisfactory character of most, if not all, of the processes for the direct determination of alumina in the presence of iron and phosphoric acid, and the sharpness with which both the iron and phosphoric acid can be determined, have led chemists to rely mainly on processes in which the alumina is obtained by difference. But in the modern alloys of aluminium and iron, where the aluminium may be present only to the extent of a small fraction of 1 per cent, nothing short of the isolation of the alumina itself can give satisfactory evidence of its presence.

In the course of some experiments on the electrolytic deposition of metals, we have found that it is possible to remove iron completely from its acid solution in large quantity and in short time, by a current that will not in the least affect the alumina in solution. The essential condition of success in this operation is the use of mercury as a cathode, the iron forming an amalgam with the mercury as fast as it is deposited from solution. This use of mercury was proposed by Dr. Wolcott Gibbs, in a paper read before the National Academy of Science in 1883, as a method of determining many metals by electrolysis which are not at all, or only imperfectly, deposited on a platinum cathode. It is certainly one of the most valuable and suggestive contributions to the quantitative separation and determination of metals by electrolysis that has yet been made.

* From the *Journal of Analytical Chemistry*, Vol. v., No. 8.

* Read before the American Institute of Mining Engineers, Cleveland Meeting, June, 1891.

The following are some of the experiments we have made to determine the conditions of success in the application of the method to the determination of aluminium in the presence of iron.

First, as to the completeness of the precipitation of the iron. The first attempts to determine the iron which had been removed from the solution and alloyed with the mercury showed an apparent loss, notwithstanding the fact that the iron was completely removed from solution. This was subsequently found to be due to the volatilisation of some of the mercury on drying before weighing. The amount of mercury which may be thus lost is very considerable, as the following experiments show.

About 75 grms. of mercury were put into a beaker, which was then weighed. It was washed several times with water, and once or twice with alcohol. The loss on drying different times and at different temperatures was as follows:—

Time of drying.	Temperature.	Loss, Grm.
10 minutes.	140° C.	0.0096
"	100°	0.0043
"	"	0.0028
"	"	0.0030
"	"	0.0030
"	"	0.0025
2 hours.	70°	0.0040
5 "	"	0.0120
20 "	"	0.0520
48 "	25°	0.0030
48 "	24°	0.0025
24 "	"	0.0007
24 "	"	0.0012
48 "	"	0.0042
48 "	"	0.0033

But it is, in fact, only necessary to heat the mercury for about two minutes at a temperature of 100° C. to free it completely from moisture, and in this time the loss is very small. The following are the amounts lost in nine experiments under these conditions:—0.0002, 0.0005, 0.0005, 0.0003, 0.0008, 0.0005, 0.0002, 0, 0, an average of 0.00033 grm.

There seems also, at times, to be a loss not connected with the volatilisation of the mercury, which, possibly, may be due to impurities in the mercury—metals, for instance,—which are dissolved out by the acid, and not precipitated on the mercury again. On this account it is desirable, in cases where the process is used to determine iron or other metal, to have a blank beaker in the circuit, containing only the mercury and dilute sulphuric acid, and to add any loss which may be found in this beaker to the amount found in the others in the series.

The following are a series of results obtained by electrolyzing a solution of ferrous ammonium sulphate, slightly acidulated with sulphuric acid.

Iron taken. Grm.	Iron found. Grm.	Loss of weight in blank. Grm.	Iron found + loss in blank. Grm.
0.2260	0.2254	Not made	
0.3727	0.3725	"	
0.3080	0.3089	"	
0.3238	0.3232	"	
0.0647	0.0632	0.0020	0.0652
0.0647	0.0634	Not made	
0.0647	0.0649	0.0000	0.0649
0.0647	0.0635	Not made	
0.0604	0.0602	0.0003	0.0605
0.0604	0.0608	0.0003	0.0611
0.3020	0.3008	0.0003	0.3011
0.3020	0.3000	0.0003	0.3003

The best conditions for the rapid precipitation of the iron are a strong current (about 2 amperes, or 20 c.c. of electrolytic gas a minute), a nearly neutral solution of small bulk, a large amount of mercury (not less than fifty

times the weight of the iron to be precipitated), and a large anode of platinum. The mercury cathode is brought into the circuit by means of a platinum wire enclosed and fused into one end of a glass tube, which passes through the liquid. It is of advantage to pour mercury into this tube to the depth of an inch, in order to weight it and make the connection with the mercury cathode more stable.

By observing the above conditions it was found practicable to precipitate 10 grms. of iron in from 10—15 hrs. The iron amalgam may contain as high as 10 per cent of iron. On standing a long time exposed to the air, the iron separates out as a black powder, which may be removed from the mercury by agitation with water. Mercury which has been used for iron precipitations may be purified by removing the greater part of the iron amalgam by filtration through chamois skin, and then passing air through the filtered portion, as recommended by J. M. Crafts.

Second, as to the behaviour of manganese in solution under the foregoing conditions. Inasmuch as manganese is almost always present in iron and steel, a good many experiments were made to find what becomes of it under the electrolytic conditions which we have been considering. It was found that a portion is oxidised to the dioxide, coating the platinum anode, and ultimately falling off, in great part in scales, and that a portion is reduced to the metallic state and alloys with the mercury. This fact of the reduction of the manganese was evident on electrolyzing a solution containing only dilute sulphuric acid, using as a cathode mercury which had been previously used in an experiment with a manganese solution. In a few minutes the permanganate colour appeared, and a slight coating of manganese dioxide was deposited on the anode. The experiments made to determine what proportion of manganese was reduced and what proportion oxidised were not satisfactory, but in general it may be said that about half the manganese alloys with the mercury; the other half is nearly all oxidised and is found both on the anode and in scales floating in the liquid. A small portion is always found in solution. By using both electrodes of platinum it was found possible, in the absence of iron, to precipitate manganese completely as dioxide; but the coating on the anode was never coherent when more than mere traces of manganese was present. But the danger of the re-solution of the floating particles of the manganese dioxide, together with the necessity of filtering and igniting it to the proto-sesquioxide, makes the process an unsatisfactory one for the determination of manganese. The best conditions were found to be a concentrated solution of manganese sulphate to which a little nitric acid had been added, a rather weak current, a small cathode, and a large anode.

Third, as to the influence of phosphoric acid on the precipitation of iron. Two solutions containing equal amounts of iron were electrolysed in series. To one was added 1 grm. of crystallised hydrogen di-sodium phosphate, and to the other dilute sulphuric acid. When the iron was all precipitated, the beakers with the mercury, together with the glass tubes containing the platinum wires, were weighed, and found to have gained, respectively, 0.1290 and 0.1275 grm. To a solution of 3 grms. of iron in sulphuric acid, 0.1935 grm. crystallised hydrogen di-sodium phosphate was added, equivalent to 0.0167 phosphorus. After the iron was completely removed from the solution, the phosphoric acid was precipitated by magnesium mixture and 0.0163 grm. phosphorus obtained. A duplicate experiment gave 0.0161 grm. phosphorus. A third experiment with the same amount of iron gave, under like conditions, 0.0064 grm. phosphorus when 0.0068 was added. From the experiments we may conclude that the separation, by this electrolytic method, of iron and phosphoric acid in solution is satisfactory.

Fourth, as to the separation of iron and aluminium. Known amounts of iron and aluminium in solution to-

gether as sulphates were electrolysed, and, after all the iron had been deposited, the alumina was precipitated by ammonia. Following are two results thus obtained:—

Alumina taken. Grm.	Alumina found. Grm.	Iron taken. Grm.	Iron found. Grm.
0·0283	0·0286	0·2286	0·2277
0·0142	0·0142	0·2286	0·2283

The iron, determined by weighing the mercury after electrolysing the solution, includes in both cases a blank of 0·0020 grm., which was the loss of a mercury cathode in the same series, when dilute sulphuric acid only was electrolysed.

The process was now tried under the conditions which would obtain in the determination of aluminium in iron and steel, namely, known amounts of aluminium sulphate were added to a known amount of steel. After much experimenting the following procedure was adopted as being the most uniformly satisfactory.

Dissolve 5—10 grms. of iron or steel in sulphuric acid, evaporate until white fumes of sulphuric anhydride begin to come off, add water, heat until all the iron is in solution, filter off the silica and carbon, and wash with water acidulated with sulphuric acid. Make the filtrate nearly neutral with ammonia, and add to the beaker in which the electrolysis is to be made about one hundred times as much mercury as the weight of iron or steel taken. The bulk of the solution should be from 300—500 c.c. Connect with the battery or dynamo current in such a way that about 2 amperes may pass through the solution over night. This we have generally accomplished by using three lamps of 32-candle power arranged in parallel on an Edison circuit. In the morning the solution is tested for iron, and, if necessary, the electrolysis is continued after adding enough ammonia to neutralise the acid that has been set free by the deposition of the iron. The progress of the operation may be observed by the changing colour of the solution. At first it becomes darker in colour near the anode; after five or six hours it is nearly colourless, and finally becomes pink, from the formation of permanganate.

When the solution gives no test for iron, it is removed from the beaker with a pipette while the current is still passing. When as much has been removed as possible without breaking the current, water is added, and the operation continued until the acid has been so far diluted that there is no danger of dissolving iron from the mercury. The anode is now taken out and the mercury washed with water until the last traces of the solution have been removed from it. After filtering, to remove any flakes of manganese dioxide which may be suspended in the solution, sodium phosphate is added in excess and ten grms. of sodium acetate. The solution is now made nearly neutral with ammonia and boiled for not less than forty minutes. The precipitate of aluminium phosphate is then filtered off, ignited, and weighed. It should be white after ignition. If it has more than the faintest shade of colour it must be dissolved by fusing with acid potassium sulphate, and again electrolysed for two or three hours. The second precipitate has been found to be always white without a trace of iron, but in general we have found the first precipitate to be free from iron or to contain such a minute amount that the second treatment is not necessary. We have determined that 0·0003 grm. of iron will give a decided red colour to 0·0076 grm. of aluminium phosphate. The precipitate of aluminium phosphate, produced as above, does not always have the composition $\text{Al}_2\text{O}_3, \text{P}_2\text{O}_5$. Our analyses of it go to show that the formula $7\text{Al}_2\text{O}_3, 6\text{P}_2\text{O}_5$ more nearly expresses its average composition, and in those cases in which the amount of phosphoric acid and alumina have not been actually determined in the precipitate, we have assumed this composition, which is equivalent to 24·14 per cent of aluminium in the precipitate.

It is necessary to boil for at least forty minutes to

precipitate completely the aluminium phosphate, and excessive washing of the precipitate should be avoided.

The following table gives the result obtained in determining by the above process the aluminium added in known amounts to solutions of steel:—

Steel taken. Grms.	Percentage of aluminium added.	Percentage of aluminium found.
5	0·39	0·36
5	0·39	0·38
5	0·39	0·38
5	0·39	0·38
5	0·39	0·37
5	0·043	0·045
5	0·043	0·041
5	0·043	0·049
5	0·043	0·048
10	0·027	0·015
10	0·200	0·160
10	0·046	0·044
5	0·085	0·088

A blank experiment with the same steel, without the addition of any aluminium, gave a precipitate of aluminium phosphate equivalent to 0·004 per cent of aluminium, which has been deducted from the results in the above determinations. This small amount came, doubtless, from the reagents and the glass vessels used, and may have been partly silica. This correction should be made in all cases where the amount of aluminium is very small.

A sample of Mitis steel analysed by this method gave the following result:—

Steel taken. Grms.	Aluminium found. Per cent.
4·4260	0·014
4·4260	0·013
12·6650	0·014

A sample of "aluminium physis" used in the preparation of Mitis castings gave as follows:—

Iron taken. Grms.	Aluminium found. Per cent.
1·6130	6·28
0·4030	6·52
0·4030	6·22

A sample of pig-iron to which aluminium had been added in re-melting gave as follows:—

Iron taken. Grms.	Aluminium. Per cent.
1·4576	0·789
1·8167	0·806
1·6390	0·794
1·6130	0·802

It might be thought that the process would be simplified by reducing the iron to the state of protoxide, and then precipitating the alumina as basic acetate, subsequently removing by electrolysis the small amount of iron precipitated with the alumina. A number of experiments proved, however, that this modification not only gave less accurate results, but involved much more work than the precipitation of all the iron by electrolysis. When the iron is all removed over night without involving any work on the part of the analyst, it is surely superfluous to go through a more or less tedious chemical operation to remove a part of the iron.

It is obvious that this process of electrolysis with a mercury cathode may be of value in other analytical operations in which the removal of the iron would be of advantage; as, for instance, in the determination of phosphoric acid by magnesia.

THE CARBAZOL METHOD FOR NITRATES IN WATER ANALYSIS.

By W. P. MASON.

So far as I am aware, no note is on record calling attention to the influence of temperature upon the results obtained by this method. Experimenting with solutions of potassium nitrate, containing 3.5 parts nitrogen per million of water, chilled to various temperatures, it was found that the cold solutions darkened much more slowly than the warmer ones. When the chilling was carried some degrees below zero the green colouration appeared very gradually indeed. It follows from this that the same precaution must be taken as when "nesslerising" for ammonia, namely, the standards and the solutions of unknown strength must be operated upon at the same temperature. It appears to be immaterial whether the tubes be cooled immediately, upon addition of the strong sulphuric acid, or be permitted to cool gradually before the carbazol solution is added. As has been already stated by Hooker, the carbazol solution was found to act better after its original yellow colour had passed into an olive-green; and, if kept in a stoppered flask, remained in good condition for use for forty-eight hours.

After very careful examination as to delicacy and uniformity of results, I must confess to some disappointment in the method.

Rensselaer Polytechnic Institute,
Troy, N. Y., Oct. 1, 1891.

NOTE ON THE INFLUENCE OF LIGHT UPON EXPLOSIVE GASES AND UNSTABLE COMPOUNDS.

By H. N. WARREN, Research Analyst.

THE apparatus employed in these experiments consisted of a powerful 15-inch lens, the light being supplied both by the lime burner and also by the combustion of magnesium. When a mixture of hydrogen and chlorine was brought under the influence of the former, combination took place, with explosion after a few minutes' interval; but when a ray of the latter was used almost instantaneous explosion followed. Rays of light of different colours were employed, consisting of red, green, and yellow; in each case the explosion was considerably retarded. In the case where a bright red beam was allowed to impinge, combination took place very slowly, amounting to the faintest explosion only.

Small quantities of chloride of nitrogen, as also iodide of that element and auric fulminate, were similarly treated, providing almost identical results.

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SCIENCE IN OUR MEDICAL SCHOOLS.

THE Introductory Addresses delivered at the re-opening of the London Medical Schools contain some utterances which, to those who long for a reform in higher education, appear not unpromising. Sir G. M. Humphry, F.R.S., is reported (*Medical Press*) to have said:—"I well remember the new life of joy that opened upon me when, at the age of sixteen, I passed from the drudgery of Latin and Greek and the other ordinary school subjects, to the study of the elementary facts and theories of physics and chemistry, and felt the glowing light of natural science dawn upon me, and realised the glorious liberty of walking in that light." He continues, speaking of the love of knowledge, "No human being is without that love; it is the heritage of everyone, and, damped though

it be by school routine and examination dread, it cannot be quite killed. . . . The food which it requires, and upon which it flourishes best, is *fresh* knowledge." By "fresh knowledge" the speaker can only mean research, investigation as contrasted to the mere getting up what others have learnt already.

Yet again, the speaker declared "that which raised Newton, Darwin, and Hunter above the level of ordinary men, and made each so great a force in advancing science and thought, was the combination in each of unusual thinking or reasoning powers with that of careful observation." How sad, then, that our ordinary college curricula do so little to develop these powers.

As to the importance of scientific training for the many outside the professional classes, Prof. Victor Horsley, F.R.S., said at University College:—"The fact is that numbers of the public, especially of the highest and lowest classes, who for different reasons are the farthest removed from Science, are easily deceived by such abominations as the Mattei treatment, the faith-cure (there is also a scare-cure), and electropathic belts."

From such delusions only the scientific spirit can set us free, and hence we need not be surprised that quacks of all grades and kinds—of whom the quack medical is merely a single type—dread the cultivation of Science. Literary culture they do not dread. In fact, men of the highest standing in the "humanities" imbibe and propagate reigning delusions.

But not all the speakers at these re-openings seem to have felt the paramount importance of Science. Mr. H. Juler, F.R.C.S., is reported to have said, at St. Mary's Hospital, that to the embryo physician "previous education and training, *especially* in classics, mathematics, English, French, and German were of great assistance; but, in *addition* to these, a good practical knowledge of biology, chemistry, and physics were most essential." The *italics* are our own. Here it seems that the speaker gives a first place to words, and to the knowledge of things a mere additional rank.

In thus glancing over the medical papers we have met with a few painful facts. We learn with regret that the "Anti-vivisection" epidemic, which we had hoped was extinct, has attacked an eminent divine in a violent form. We are not a medical nor a biological organ, but, on the principle "*Jam proximus ardet Ucalagon*," we cannot view this recrudescence of a moral malady with indifference. Who knows whether some hysterical conscience will not suddenly denounce research in chemistry and physics?

THE SELF-PURIFICATION OF RIVERS.

IN the sanitary section of the German Congress of Naturalists and Physicians, Prof. von Pettenkofer read an important paper on this subject. His more immediate purpose was to inquire whether the sewage of Munich could be safely allowed to flow without treatment into the river Isar. A water is said to be polluted when it is no longer clear and inodorous, when fishes and plants perish in it, and when it contains more organic matter and less oxygen than are to be found in the unpolluted portions of its flow. Such contamination is essentially different from the transient turbidity due to heavy rains or to melting snow. Still, even the permanent pollutions disappear in the further course of the river bed, not merely by deposition, but by other agencies to be discussed below. Here the rapidity of the stream and the quantity of the water exert, as it is well known, a preponderating effect.

The most formidable impurities are considered to be the putrescent refuse which flows out of the sewers, and which very quickly produces an offensive odour at the places where they accumulate. In this respect very peculiar prepossessions have been developed; human

excretions are regarded as more dangerous than those of the lower animals; the overflow of cesspools is pronounced less objectionable than the discharge from water closets, and urine is declared less formidable than solid excrement. But the accurate researches of Von Voit have shown that an adult well-fed human being voids in 24 hours 1254 grms. urine, and only 31 grms. solid excreta. These figures are considerably reduced by the circumstance that the excretions contain not less than 92 per cent of water.

On evaporation the urine leaves only 65 grms. solid matter, including 20 grms. ash, and the excrement only 34 grms. containing 6 grms. ash. If we deduct the mineral matter, consisting of sodium chloride, alkaline chlorides, and earthy alkalies, which are perfectly harmless, the daily contaminations of the river amount only to 73 grms. per head. It is decidedly more difficult to estimate the impurities which the sewage contains in the form of commercial and industrial refuse, which play a very important part. According to the Saxon Board of Health (*Landes Medicinal Verwaltung*), the river-pollution due to industrial refuse is 93 per cent, as against only 7 per cent arising from sewage properly so-called.

Von Pettenkofer has for many years given his attention to this question, and has continually had researches conducted by his pupils. But nothing has hitherto altered the opinion which he expressed long ago that sewage may without hesitation be permitted to flow into a river, if its volume is not more than 1.15th that of the river water, and its rate of flow decidedly greater than that of the current. Nevertheless, most German local authorities prohibit in every case the introduction of crude sewage into a river. The speaker has encountered no little hostility, as he gave an opinion opposed to this practice for the waste waters of the city of Munich. To come to a decision on this question we must take the circumstances of the case into exact consideration.

Munich counts at present 280,000 inhabitants, who, if we set out from the figures of Von Voit as above cited, and overlook the fact that women, children, and the aged excrete less matter than adult and properly fed men, void daily 20,440 kilos. of putrescent organic matter, which in the course of a year gives the mighty total of 7,458,000 kilos.

If we start in the first moment at these figures the picture changes as soon as we take into account the volume of water flowing in the Isar. According to accurate observations this river discharges 40 cubic metres of water per second, or daily 3,456,000 cubic metres. If the quantity of pollution is weighed against this figure the former is only $\frac{1}{100,000}$, or 6 m.grms. per litre. This pollution is so inconsiderable that it cannot be detected by the eye if a corresponding mixture is made up experimentally. But it is also not permanent, for at Ismaning, 7 kilos. below Munich, the sewage influx is no longer to be detected, although now more than half the closets have been connected with the sewers. Still less is a detection of sewage matters to be detected bacteriologically or chemically at Freising, 33 kilos. below Munich. On January 21st of this year, samples of water were drawn from the Isar, both above Munich and at Freising. The former contained per litre 243 m.grms. solid residue, the second 252. The former required for oxidation 1.4 m.grm. oxygen and the latter 1.6. These differences are so small that they fall within the limits of experimental error. In this summer specimens were drawn on June 18th, July 22nd, and August 2nd, which gave on evaporation a mean residue of 197 m.grms. per litre, and required for oxidation 2.3 m.grms. oxygen. The circumstance that in winter the organic matter is one-half lower, and the inorganic matter higher than in summer, is explained by the affluents which feed the Isar. The melting snows and the heavy rains increase the organic matter in a manner easy to be understood.

The bacteriological researches conducted by Prausnitz equally prove the purifying power of the Isar. The

number of 198,000 bacteria per c.c. found at the mouth of the Munich sewer was reduced at Ismaning to 15,231, and at Freising to 3602. These results agree with those of other investigators. Fränkel found in the water of the Spree above and below Berlin 6000 bacteria per c.c., but in the city a million. The mere number of bacteria found has, however, no sanitary significance, since the bacteria found in the water are almost exclusively harmless, and, indeed, destroy the pathogenic microbia in the struggle for existence. In fact, if we except the apparently untrustworthy statements of some French investigators, pathogenous bacteria have hitherto never yet been found in river water.

If they were present and, in spite of the enormous dilution, were able to produce infectious diseases, this would have become manifest by statistical facts. It might have been assumed formerly, when Munich was a notorious nest of typhus fever, that this was the cause of the cases of typhus in the towns situated lower down the Isar. But Munich has been almost freed from typhus by sanitary improvements, whilst the above-mentioned smaller towns in the Isar valley which have not amended their hygienic arrangements are still as abundant in typhus cases as they were in times when it was attempted to blame Munich for the infection.

If the self-purifying power of the Isar is thus demonstrated the question arises how it is effected. This has been repeatedly ascribed to subsidence, but nothing save Isar gravel has ever been found by dredging below Munich. As little has the author obtained any kind of deposit by allowing sewage to trickle continuously over a moving channel filled with gravel.

Von Pettenkofer ascribes the purifying action of rivers solely to the oxygen dissolved in the water in a free state or separated from organisms. In the latter respect the green algae and other chlorophyllic or even non-chlorophyllic plants come prominently into consideration. It is therefore urgently requisite to preserve this vegetation, which may be destroyed by a too great concentration of the water to be purified, just as a field may be damaged by over-manuring. To this end the oxygen in the water, which is absorbed by the plants and given off again, must be present in sufficient quantity. On the other hand, industrial waste waters which destroy aquatic vegetation must not find entrance into the river unless previously purified. What part is played by oxygen may be observed in aquaria, where the sea water does not need to be renewed for months if air is passed through. The water remains clear, although it receives the excretions of the animals present and many residues of their food. But it is at once rendered turbid by bacteria if the supply of air ceases.

On account of the clearly demonstrated self-purification of the Isar, Von Pettenkofer declines to take upon himself to delay or complicate the domestic drainage and sewage of Munich, so important from a sanitary point of view, by the demand for irrigation fields, which is not easy to fulfil. He leaves to the future the installation of such fields, the use of which he does not deny, but the management of which should not be imposed upon the towns, but left to the agriculturists.

Von Pettenkofer concluded his lecture amidst general applause with the recommendation that the self-purifying power of rivers should be closely examined in as many places as possible.—*Chemiker Zeitung*.

Remarks on Hiepe's Paper "A New Use of Oxygenated Water in Analysis.—Mann (*Chemiker Zeitung*).—Hiepe regards the frequent presence of magnesium sulphate in oxygenated water as quite inexplicable. Mann informs him that oxygenated water prepared with barium dioxide contains barium chloride, which must be absolutely removed. In practice it is often eliminated by a cautious addition of magnesia.

NOTICES OF BOOKS.

The Perplexed Farmer: How is he to meet Alien Competition? Three Lectures, given at Brussels before the Belgian Royal Central Society of Agriculture, by GEORGES VILLE. Translated from the Fourth French Edition, with additional matter supplied by the Author, by WILLIAM CROOKES, F.R.S., V.P.C.S., &c. London: Longmans, Green, and Co.; and New York.

For a just appreciation of this work the reader will do well to bear in mind the first sentence of the Preface to the English edition. M. Ville's book does in fact consist of two portions, interwoven indeed, but so different in their character that the one part, the technical agricultural teachings, will be—or at least should be—warmly greeted by everyone who feels an interest in agriculture. Those who have met with the author's larger work, "Artificial Manures" (Longmans and Co.), will find the views laid down in that book here compactly re-stated, with all the additional weight which the experience of the last decennium has supplied. In his former work the author insisted that among all the ingredients of an arable soil, four only—phosphoric acid, nitrogen, potassa, and lime—need to be constantly supplied, the others, though necessary, being always present in sufficiency, if not in superabundance. Here it may be remarked that his teachings differ from English practice. We find nitrogen, phosphoric acid, and potassa always necessary, but we consider that lime is found in plenty in almost all soils. If it be contended that such lime may not be in a form available for vegetation, we reply that it is evidently dissolved by the rain and the carbonic acid of the atmosphere, as the springs and the streams of the limestone, and the chalk districts, are invariably "hard," from the presence of lime in solution.

But this matter does not call for discussion here. M. Ville, to meet some rather obsolete objections against chemical manures, shows the relation which they bear to farmyard manure. This substance, the alpha and the omega of traditional rule-of-thumb agriculture, is, in fact, like a chemical manure of very low quality.

Suppose we take 100 tons of farmyard dung, we find in it 80 tons of water, 13.29 tons of woody fibre, 5.07 tons of minerals which the soil does not need, and only 1.64 tons of the active matters—nitrogen, phosphoric acid, potash, and lime! Now it is evident that 1.64 tons of the really active matter can be bought for less money than the 100 tons of farmyard manure. Hence the farmer who buys and keeps up a stock of cattle merely or mainly to produce dung is painfully like an iron-master who should plant and maintain forests in order to supply his furnaces with fuel.

M. Ville must not be misunderstood. He does not decry cattle-feeding as a source of milk, meat, &c. He urges that the dung of animals kept for such purposes should be applied to the land after being duly fortified with phosphates, potash, or nitrogen, as it may be found needful for the requirements of any given crop. But he insists that farmyard manure is not a necessary factor for the production of crops, which can be grown as well, and often more economically, without it. Above all, he protests against the notion that matter obtains any mysterious occult value by passing through the bodies of animals. There is nothing in the dung which there was not in the food of the ox, horse, or sheep. And there is nothing in the food, be it grass, corn, or the like, which was not in the soil upon which the herbage, &c., grew. It is painful in these days to find agricultural authorities still advising farmers to buy "good feeding stuff" rather than superphosphate, salts of potash, sulphate of ammonia, or nitrate of soda.

But we must hasten on. Of the three substances—nitrogen, potash, and phosphoric acid—there is, according to M. Ville, or rather according to the facts of Nature, always some one which more especially influences some

given crop, and which the author calls the *dominant* of that crop. Thus nitrogen, in the form of sulphate of ammonia or of saltpetre, is the dominant of wheat, hemp, and natural meadows; potash plays a corresponding part for peas, potatoes, lucerne, clover, and the vine. The dominant of the sugar-cane and the turnip is phosphoric acid, in the state of superphosphate, basic slag, &c. The ignorance or the neglect of this doctrine leads to much useless expenditure. Thus if we wish for a very fine crop of peas, and give accordingly a rich nitrogenous dressing, we do not recover the extra cost of the manure. If we add no nitrogenous manure at all, we get substantially as good a crop as if we had applied it. It may here be mentioned that peas, like many other leguminous plants, are able to appropriate the nitrogen of the atmosphere through the means of the small tubercles perceived on their roots, which abound with certain micro-organisms. More than this, upon clover, &c., the action of nitrogenous manures is actually hurtful.

A principle upon which M. Ville lays great weight, and which seems to have before it in agricultural practice a vast future, is "sideration." As every physicist knows, the sun pours down upon any given plot of land an amount of *vis viva* greatly in excess of the quantity actually utilised in the cultivation of the soil. By way of turning to account a part at least of this wasted energy, he advises that some of the plants which absorb the nitrogen of the atmosphere—such as clover—should be sown among corn or upon fallows. One or two crops of clover may thus be ploughed in, to the enormous increase of the fertility of the soil.

Another subject to which M. Ville has devoted his attention is what he calls *eugenism*—i.e., the selection and varieties of plants which yield earlier, heavier, and more resistant crops than do others.

The work before us—setting aside the somewhat questionable political economy with which it is interwoven—is not only useful but profoundly suggestive, and deserves a careful study not only in the library, but in the experimental field. It is perhaps not too much to hope that M. Ville's labours may usher in a new era for agriculture.

A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali with the Collateral Branches. By GEORG LUNGE, Ph.D., Professor of Technical Chemistry at the Federal Polytechnic School, Zurich (formerly Manager of the Tyne Alkali Works, South Shields). Second Edition, Revised and Enlarged. Vol. I.—Sulphuric Acid. London: Gurney and Jackson. 8vo., pp. 940.

(FIRST NOTICE.)

In the Preface of this work we find the following significant passage:—"The manufacture of chemicals has made enormous strides forward, both in quantity and quality, in France, and even more so in Germany. Many of the chemicals of these countries outstrip those of English works in purity, and their plant and their processes are frequently superior to those used in the majority of English works. Everybody knows how this has come about. The foreign chemists and manufacturers have looked all around, not merely in their own countries, but wherever they could find improved methods and apparatus, and upon the practical knowledge thus gained they have brought to bear the scientific training they had received at their universities and polytechnic schools. Thus they have already, in many fields formerly remunerative to British manufacturers, distanced the latter, immensely aided though they are by their long occupation of the ground, and by permanent natural advantages, such as cheapness of coal and freight." "This," he continues, "is likely to go on to an increasing extent if many British manufacturers decline to profit from a scientific study of their respective branches. This is all the less

excusable as England from of old has been a stronghold of scientific chemistry, and can hold its own against the whole world in that respect."

The moral involved in this passage does not need to be enlarged upon; it must be patent to every man who is not wilfully blind.

The present edition of Dr. Lunge's work is by no means a mere reprint of the former. Much that is now superseded has been eliminated, and is now merely referred to as to be found in the first edition. On the other hand, so much new matter has been added that the text is increased from 658 pages to 903 pages, and the engravings from 309 to 374, of which more than 150 are new. The author is in fact fully justified in calling it a new work, for which the first edition has served as the basis.

After giving a history of the manufacture of sulphuric acid, and a brief sketch of its general principles, the author passes to a survey of the raw materials employed. As regards brimstone, the Sicilian deposits still form the main source, though it is calculated that they will be exhausted in about sixty years. We find no mention of a large deposit of native sulphur said to have been discovered in New South Wales. By 1852 brimstone had been discarded in Lancashire in favour of pyrites, but it remained in use on the Tyne for a short time, though only on a small scale.

The British deposits of pyrites are not important either for quantity or quality. Cornish samples very rarely exceed 34 per cent of sulphur, and contain as much as 1.16 per cent of arsenic.

Irish pyrites are of more importance. They rarely exceed 35 per cent of sulphur, except those of Ovoca, which may reach 44 per cent. Irish ores are no longer burnt in England, on account of their exceedingly dense structure, — especially the yellow ore, — and it is very difficult to burn them reasonably clean, and even their analysis is a tribulation. The best pyrites of home origin is that from the Cae Coch Mine in Wales, which yields 48 per cent of sulphur, and is entirely free from arsenic. Unfortunately the supply is not large. It serves for manufacturing very pure oil of vitriol.

The most important German pyrites bed is at Meggen, in Westphalia. It is said to be quite free from arsenic — which Dr. Lunge queries — and to contain 47.5 per cent of sulphur. A drawback to the German ores is their proportion of zinc, which holds back a considerable quantity of sulphur in the state of sulphate. In Silesia 14 per cent is allowed as a maximum, and beyond this 1 per cent of sulphur is deducted on the invoice for each per cent of sulphur.

Norwegian pyrites contain mere traces of arsenic and burn clean, but they are in little favour, as their proportion of copper is too low to be worth extraction.

British acid-makers now principally burn Spanish and Portuguese ores from Huelva, the Rio Tinto, &c. These pyrites contain from 46 to 50 per cent of sulphur and from 3 to 4½ per cent of copper.

Dr. Lunge appropriately denounces the Cornish copper-assay, "a process of dry assaying only known to a few assayers living at Redruth and other places in Cornwall, the great inaccuracy of which is perfectly well known to all the parties concerned; it shows, for instance, only 2 per cent if 4 per cent are actually present. The price to be paid for the copper in the ore, by Cornish assay, is sometimes higher than the value of a similar quantity of copper metal. This remarkably irrational system has not hitherto been done away with for sales."

One of the greatest trials of a young chemist in the Lancashire district was to make his results, as obtained by modern accurate methods, coincide with those of this absurd process.

Many American pyrites have the advantage of being free from arsenic.

A very objectionable property of certain Spanish ores, as also of that from the Goshen Copper Mine, Co. Cork

is that they explode in the kilns and choke up the burners with fine dust.

The author explains why rich ores, wherever obtainable, have quite superseded poorer qualities. The cost of breaking and burning a ton, say, of 35 per cent ore, as well as the wear and tear of plant and the waste in the cinders, are as great as on a ton of a 45 per cent ore, whilst the returns are much less.

The instructions for the analysis of pyrites are full and excellent, and the attention of the operator is called to certain possible sources of error, such as the presence of nitric acid or a nitrite in the solution of the ore, and of ferric oxide or sulphate in the precipitate.

Department of Agriculture, Victoria. Report of the Department of Agriculture for the Year 1889—90. Bulletin No. 12. Melbourne: R. S. Bain.

THIS report is, upon the whole, highly satisfactory as showing an earnest desire to utilise the natural advantages of Victoria.

Mr. A. N. Pearson, F.C.S., the agricultural chemist to the Colony, is, with his two assistants and two pupils, busily engaged in the analysis of soils, manures, vegetable products, water, &c.; as also in experimenting on the preservation of fruits and milk, on the application of manures, and on the extermination of rabbits; 196 samples of soils, clays, &c., have been examined, 76 manures, 1586 samples of water, and 4 insecticides. The waters are classified as for irrigation, for domestic use, for farm and boiler work, samples of the Yarra water taken to decide its value for irrigating the Botanical Gardens.

Special attention is now being given to the growth of perfume plants, for which many parts of Australia are well adapted. The kinds of soil suitable for jasmine, tuberose, oranges, almonds, &c., are duly indicated. Soils are analysed free of charge, as are also manures if for farmers, but fees are charged to merchants and manufacturers.

Wattle bark from two-year-old trees was found to contain 46.47 per cent of tannin, whilst that from three-year-old trees gave 47.14. But the extract of the latter was the palest, which is of course an advantage both for dyeing and tanning purposes.

Experiments on the use of salicylic and boric acids for the preservation of foods led to condemnatory results.

Attempts are being made with a fair prospect of success to introduce the condensed milk industry. The native product is found richer in cream by nearly 3 per cent than the Swiss "Dairy Maid Brand."

Test-plots, for deciding the efficiency of manures, as proposed by M. Ville, are coming into favour.

We cannot express approval of the attempts to introduce the beet-sugar manufacture. There is plenty of land in Australia well adapted for the growth of the cane.

The entomologist to the department, Mr. A. N. Pearson, is fully employed in examining insects injurious to fruit-trees and experimenting on the diseases which they occasion. In this respect he works hand in hand with Mr. D. McAlpine, the vegetable pathologist and fungologist.

Much money and trouble are being expended in extirpating the Californian thistle, which has been introduced either by carelessness or criminal folly.

The cultivation of fruits is extending, and the produce is being exported to England both in the fresh, dried, bottled, and candied states. Australian fruits have the advantage that they reach English ports in late winter and spring, when European and American produce is scarce.

Butter, as an export from a sub-tropical country, may surprise us. But the value of the dairy industry in Victoria is given as above £3,000,000 annually, being more than the production of gold. Victorian butter is pro-

nounced by buyers in the London market second only to the best.

Attempts at the cultivation of dye-warens we can scarcely recommend. Many would doubtless grow to perfection in Victoria. But the demand for natural dyes has been so much reduced by the coal-tar industry that their cultivation could scarcely be remunerative. This is especially the case with madder.

CORRESPONDENCE.

BEHAVIOUR OF BUTYRIC ACID WITH ALKALINE PERMANGANATE.

To the Editor of the Chemical News.

SIR,—In reference to my previous note upon the above subject (CHEMICAL NEWS, vol. lxiii., p. 111) I have been induced to further investigate this extremely interesting question, for, as far as I am aware, it is the first recorded instance of the whole of the carbon being retained, no carbonic dioxide being produced in the reaction; and, further, because one of my critics went so far as to prognosticate that I should have to retract my statement, at the same time quoting from Beilstein's "Ag. Chem.," vol. i., p. 402, "that it was a well-known fact that butyric acid, when boiled with alkaline permanganate, resolved itself into carbonic acid" (Analyst, vol. xvi., p. 50).

Coinciding with the above, Mr. A. H. Allen has introduced me as an authority to the members of the British Association, at their Cardiff Meeting (as reported in the CHEM. NEWS, vol. lxvi., p. 179) as follows:—"That it was erroneous was already rendered extremely probable by Mr. Hehner's failure to obtain any traces of oxalic acid from butyric acid by treatment with permanganate" (CHEM. NEWS, vol. lxiv., p. 182).

In the *Zeitsch. f. Angew. Chem.*, 1891, p. 400, there is an article headed "The Estimation of Glycerol by Benedikt and Zsigmondy's Method," by C. Mangold. The author, after describing his simplifications of Benedikt and Zsigmondy's method, goes on to state "Butyric acid yields oxalic acid only when boiled for a considerable time with an excess of alkali and potassium permanganate,"—exactly what I have already announced, and the discoverer of this eccentric but wonderful reaction has his work unexpectedly confirmed. The question does not even end here, for in the August number of the official Journal of a semi-trade society there appears an abstract of C. Mangold's paper already referred to; but all mention of the formation of oxalic acid from butyric acid, in the manner described, is carefully suppressed, the abstractor's initials being O. H.

Mr. Allen charges me with having stated that "tallow required 23 per cent of caustic potash (KHO) for its saponification, against 19.3—19.8 per cent as the united experience of numerous other observers" (CHEM. NEWS, lxiv., p. 182). I never said or wrote anything of the kind; the statement is purely a misrepresentation. He quotes me as an authority to support his own opinions, when it suits himself; the next minute he abuses me. He also refers to the bichromate method for the estimation of glycerin, but the same objection applies to it, as later research has proved conclusively that butter contains a volatile fatty acid which readily reduces acid bichromate, not to mention castor oil, which is said to contain isobutyric acid.

The butyric acid and permanganate reaction is extremely interesting and also eccentric, but with care theoretical results can be obtained; and in saying *Ad revocor* to my critics I have nothing to retract; it is they who must again recant.—I am, &c.,

WILLIAM JOHNSTONE.

13, Fish Street Hill, E.C.,
October 10, 1891.

MR. ALLEN AND THE ISOGLYCERIDE THEORY.

To the Editor of the Chemical News.

SIR,—From the report of Mr. Allen's paper published in the last number of the CHEMICAL NEWS, I perceive that in my absence from the meeting of the British Association that gentleman has made a very extraordinary statement, which would not have passed unchallenged in my presence. I quote the following passage: "I believe Messrs. Wanklyn and Fox have never published a single original experiment in support of their assertion that the proportion of glycerin yielded by saponification of butter and other fats exhibits any grave departure from the amount required by the accepted views of their constitution."

Now, so far from there being any ground for that statement of Mr. Allen's, the very reverse is notoriously true. At a meeting of the Society of Chemical Industry I did publish an original experiment in support of my view, and, strange to say, Mr. Allen was present, and actually took part in the discussion. The paper was published by the Society of Chemical Industry, and the following is an abstract. I operated upon 50 grms. of dry butter-fat, and saponified with a weighed excess of lime, proving that saponification was complete by showing that the lime had absolutely lost its causticity, and that the butter had ceased to exist as butter, inasmuch as 300 c.c. of boiling alcohol dissolved no butter out of the residue; and having proved that complete reaction had taken place I sought for the resulting glycerin, and obtained only 3.1 grms. instead of double the quantity, as the commonly received theory requires. I believe that chemists will find great difficulty in resisting the conclusion which follows from this experiment. Whether Mr. Allen will be satisfied by it I cannot tell; but until he has given some explanation of the extraordinary assertion which I have quoted, I shall consider myself relieved from the necessity of noticing anything else in his paper which deals with a subject on which I possess special information.—I am, &c.,

J. ALFRED WANKLYN.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 13, September 28, 1891.

This issue contains no chemical matter.

Moniteur Scientifique, Queneville.
Series 4, Vol. iv., Part 2, No. 587.

Determination of Minute Quantities of Aluminium in Irons and Steels.—J. E. Stead.—From the *Journal of the Society of Chemical Industry*.

New Method for Determining Aluminium in Ferro-Aluminium and Steel.—A. Ziegler (*Dingler's Journal*).—This paper will be inserted in full.

New Process for Determining Pure Glycerin in Commercial Glycerin.—C. and Ch. Deiss (*Römer's Journal*).—This process is founded upon the fact that a given mixture of glycerin and phenol always absorbs the same quantity of water. The weight of water absorbed is proportional to the degree of concentration of the glycerin employed. To make a determination, we place in a beaker holding about 100 c.c. a mixture of 10 grms. of

the glycerin in question and 6 grms. of pure crystalline phenol. Then we drop in by means of a Mohr's burette a solution of 50 grms. of phenol and 1 litre of distilled water until there appears, on stirring, a permanent turbidity. Pure anhydrous glycerin requires to produce this result 28.15 c.c. The authors have remarked that for each additional per cent of water in the sample the number of c.c. employed diminishes by 0.39 c.c. So that if we call g the number of c.c. used, the quantity of water per cent will be shown by the formula $\frac{28.15 - g}{0.39}$. It is preferable to operate at the temperature of 11° .

Titration of Formaldehyd by means of Ammonia.—W. Eschweiler (*Chemiker Zeitung*).—G. Losekann has recently pointed out that when titrating formaldehyd with ammonia we must remember that the hexamethyleneamine formed can, in its quality of monacid base, take possession of a part of the acid by means of which we titrate the excess of ammonia. The quantity of ammonia which disappears would be for 6 mols. formaldehyd, not 4 mols., but only 3; one mol. of the acid used for the titration being neutralised by the hexamethyleneamine formed. According to the author, this assertion is inaccurate if we use methyl orange or cochineal as indicator. If we use litmus, we must not take account of the acid corresponding to the hexamethyleneamine.

Determination of Indigo for Industrial Use.—F. A. Owen (*Roman's Journal*).—One gm. of the product is dried at 100° , and the loss of weight is determined. It is then ground as finely as possible in a glass mortar, water is added, and it is rubbed up to a thin paste, which is introduced into a flask of 250 c.c. There are then added 3 grms. of zinc powder and about 6 grms. of caustic soda, the flask is filled up to the neck and agitated from time to time. After from half an hour to two hours the reduction is complete, when the liquid should be green. Fifty c.c. are then taken with a pipette, and exposed to the air for half an hour. The indigo is then thrown down with hydrochloric acid, collected upon a filter, dried at 100° , and weighed.

Researches on the Procedures for Determining Albumenoid Substances, with especial reference to Milk.—J. Sebelien.—From the *Bulletin de la Société Chimique*.

Agricultural Analyses.—H. J. Patterson.—From the *American Chemical Journal*.

Artificial Colouring Matters considered with reference to their Poisonous Properties.—This treatise does not admit of useful abstraction.

MISCELLANEOUS.

Spectroscopic Analysis.—Prof. Ostwald (*Chemiker Zeitung*), in a discourse on the progress of Physical Chemistry, delivered before the Congress of German Naturalists and Physicians, declared that, owing to the recent investigations of Baluzez, Deslandres, Kayser, Runge, and others, results have been reached which justify the most sanguine hopes. It is generally believed that all substances are dissociated in the electric arc into their elements, and that thus a spectrum of their components is obtained. All substances which are formed with absorption of heat become more permanent as the temperature rises, and inversely. In many instances this inverse case occurs, but it cannot be assumed as the universal and sole course of the phenomena.

Use of Lupins, Horse Chestnuts, and Acorns as Human Food.—At the recent Congress of German Naturalists and Physicians, P. Soltsien (*Chemiker Zeitung*) recommended the use of ammonia at 10 per cent as a suitable agent for removing tannin and poisonous alkaloids. Horse chestnuts and acorns must be previously comminuted. As lupins contain no starch, it should be

added to the purified product in the shape of ground acorns. The attempts at utilising horse chestnuts (essentially removal of sapotoxine) are not very satisfactory, as the loss of substance is very considerable. Fragments of the rind must also be removed, as they contain much tannin. Attempts to make horse chestnuts edible by roasting have not yielded good results; the sapotoxine is certainly destroyed, but the nuts cannot be eaten, as the fatty oil takes an unpleasant taste on roasting. The results which the author obtained in removing the bitterness of acorns are noteworthy. In addition to the ammonia process he obtained good results by extracting the acorns six to eight times with cold soft water, and drying immediately afterwards. The loss by this method is still too great (25 per cent), consequently Soltsien prefers to make the acorns up into a paste with milk, and allow them to ferment. The elimination of bitterness by this process is substantially perfect, and loss is avoided. Acorn meal so prepared costs at most 4d. per kilo.

Self-Acting Apparatus for Shutting off Gas-Flames.—J. Hartkorn (*Chemiker Zeitung*).—An intermediate flask is inserted in the gas-piping from which the gas reaches the flexible tube, passing to the burner through a long glass tube sliding in the stopper. Into the flask water flows with a known speed from a cistern placed at a higher level. As soon as the level of the latter reaches the lower end of the exit gas-pipe the latter is closed and the flame is extinguished.

Action of Organic Compounds upon the Alkaline Sulphohydrates.—F. Fuchs (*Monatshefte*).—The view expressed by the author in an earlier paper, that also in the oxy-acids of the fatty series only the hydrogen of the carboxyl group is replaced by a metal on treatment with an alkaline hydrosulphate, has been found fully confirmed by experiments on malic and tartaric acids. The halogeniferous monatomic phenols do not seem to act as acids.

Recognition of Diresorcine in Synthetic Phloroglucine.—J. Herzig and F. Zeisel (*Monatshefte für Chemie*).—A few milligrams of the phloroglucine in question are treated with 1 c.c. of concentrated sulphuric acid, 1 to 2 c.c. of acetic anhydride are added, and the whole is heated for five to ten minutes in a boiling water-bath. In presence of diresorcine, there appears a fine violet-blue colour. By means of this reaction, 0.4 per cent of diresorcine can be detected in phloroglucine. Pure phloroglucine, from maclurine, or obtained by means of the acetate method, or of Skraup's process, are perfectly free from diresorcine, whilst commercial phloroglucine always gives the above reaction.

Araometer for Complete Submersion.—N. Reggiani (*Atti dei Lincei*).—In this instrument the surface tension of the liquid does not interfere. Glass bodies may be loaded with platinum rings so that they remain suspended in the liquid. Or for certain purposes the author uses hollow glass globes of known specific gravity placed in the liquid in question, which is then diluted with water until the balls remain suspended. In this case corrections are needed both for the temperature and the contraction in volume occasioned on mixing the liquids.

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A METHOD FOR THE SEPARATION OF ANTIMONY FROM ARSENIC BY THE SIMULTANEOUS ACTION OF HYDROCHLORIC AND HYDRIODIC ACIDS.

By F. A. GOOCH and E. W. DANNER.

A METHOD for the separation of arsenic from antimony based upon the difference in volatility of the lower chlorides was introduced originally by Fischer.* This method of treatment consisted in the reduction of the chlorides by means of ferrous chloride and the volatilisation of the arsenic by repeated distillations of the mixture with hydrochloric acid of 20 per cent strength added in successive portions. The process has been subsequently modified by Hufschmidt† by the substitution of gaseous hydrochloric acid, introduced in continuous current into the distilling mixture, for the aqueous acid, and later changed further and improved by Classen and Ludwig,‡ who employ ferrous sulphate, or ammonio-ferrous sulphate, in place of the less easily prepared ferrous chloride. In its latest form the method is exceedingly exact, but the conditions are such that the antimony in the residue must be determined gravimetrically. It has been our endeavour to so arrange the process that the determination of the antimony may be made by a rapid volumetric method, and this we have attempted to accomplish by substituting for the iron salt, which utterly precludes the direct volumetric estimation of the antimony, another reducer—hydriodic acid—which can interfere in no way with the subsequent determination of the antimony by the well known iodometric method.

It has been shown in previous work in this laboratory that arsenic§ and antimony|| may both be reduced by the action of hydriodic acid applied under appropriate conditions. In those processes, however, it was essential that the arsenic should not volatilise, and the conditions were adjusted accordingly. In the present case we have to test the reducing action of hydriodic acid in the presence of strong hydrochloric acid and at the boiling temperature of the solution,—conditions arranged to bring about the volatilisation of the arsenic as rapidly as possible. Certain preliminary experiments gave indication that a $\frac{1}{2}$ gm. of arsenic oxide could be completely volatilised by the action of potassium iodide in excess in the manner described, and that an equivalent weight of antimonious oxide (added in the form of tartar emetic) was retained entirely in the residue under similar conditions of treatment. Moreover, it appeared that this action could be brought about in solutions measuring no more than 100 c.m.³ at the beginning and no less than 50 c.m.³ at the end of the distillation, so that a very considerable saving of time over that demanded by the process of distillation, as left by Classen and Ludwig, could be effected. Accordingly we proceeded to test the action of the hydriodic acid quantitatively, following the same general lines. The distillation apparatus consisted of a flask of 250 c.m.³ capacity, provided with a hollow glass stopper tightly fitted in a ground joint, the stopper itself being sealed upon a large glass tube bent suitably to connect the interior of the flask with an upright condenser, while through the hollow stopper, and sealed into it, passed a smaller glass tube reaching nearly to the

bottom of the flask. The arrangement was such that a current of gas entering the smaller tube would pass nearly to the bottom of the flask, and then out through the hollow stopper into the condenser, without meeting joints of rubber or cork. Into this flask was weighed, for the experiments of Table I., about a $\frac{1}{2}$ gm. of carefully re-crystallised tartar emetic, and a $\frac{1}{2}$ gm. of pure dihydrogen potassium arseniate and a gm. of potassium iodide were added in concentrated solution, the volume of liquid being made up to 100 c.m.³ by the addition of strong hydrochloric acid. A brisk current of hydrochloric acid gas was passed into the solution through the tube sealed into the glass stopper of the flask until complete saturation was effected, and then the liquid was heated and distilled in the continuous current of hydrochloric acid gas until the volume of 30 c.m.³ was reached. Iodine was evolved as soon as the liquid became warm and the greater part of it passed into the distillate with the first 10 c.m.³. When the final concentration was reached the solution was in each case colourless, but on cooling there appeared in one of the two experiments of this set a pale yellow tint, which vanished with the dilution involved in the transfer and washing from the flask previous to titration. The addition of starch to the cooled and diluted liquid developed no colour. To the liquid were added 1 gm. of tartaric acid, to keep the antimony in solution during subsequent treatment, sodium hydrate nearly to neutrality, and hydrogen sodium carbonate in excess amounting to about 20 c.m.³ of the saturated solution; and the antimonious oxide in solution was titrated by decinormal iodine standardised against tartar emetic. The details of these experiments are given in Table I.

In Table II. are comprised the accounts of experiments similar in general to those of Table I., excepting that the final volume after concentration was a little more, and the antimony was in every case oxidised in alkaline solution by standard iodine previous to the introduction of hydrochloric acid and distillation.

Table III. includes the records of experiments similar in every respect to those of Table II., excepting that, as starch showed a slight colour in the cooled liquid after distillation, the solution was treated with an excess of sulphurous acid which was subsequently oxidised exactly by standard iodine previous to neutralisation and the final titration.

The same general phenomena were observed in all these experiments, and deficiencies in the amounts of antimony indicated, whether the element was present in the lower or higher degree of oxidation before distillation, appear in all, but most notably in the results of Tables I. and II. These losses cannot be attributed, entirely at least, to mechanical transfer in the process, inasmuch as the greater losses are not associated with the greater concentrations; and, furthermore, according to our qualitative experiments made under the conditions of these determinations, no antimony, so far as we could observe, passes into the distillate. If the colouration of the liquid on cooling were due to the liberation of iodine by the action of air upon the hydriodic acid, the iodine thus set free might be counted upon to oxidise a corresponding portion of the antimony in the neutralisation, and so to occasion a deficiency in the indications of titration. Against this supposition, however, we have the evidence of experiment that the greatest losses are not found in those cases in which colour was developed in the cooling liquid. Moreover, in all cases, excepting those of Table III., starch gave no test for free iodine in the diluted liquid, though it must not be overlooked that the presence of a considerable amount of hydrochloric acid tends to impair the delicacy of the test. If, on the other hand, the colour is not due altogether to free iodine, it is difficult to account for its development, unless it is caused by the formation of antimonious iodide as the solution of strong hydrochloric containing also hydriodic acid cools. On the whole, we are inclined to attribute at least a part of the apparent deficiency to the presence, at the time of

* *Ann. Chem. u. Pharm.*, 208, 182.

† *Ber. d. Deutsch. Chem. Ges.*, xvii., 2245.

‡ *Ibid.*, xviii., 1110.

§ Gooch and Browning, *Amer. Journ. Sci.*, xl., 66.

|| Gooch and Gruener, *Ibid.*, xiii., 213.

TABLE I.

H_2KAsO_4 taken. Grm.	KI taken. Grm.	Volume		Colour		Sb_2O_3 taken. Grm.	Sb_2O_3 found. Grm.	Error. Grm.
		Initial. C.m. ^a	Final. C.m. ^a	On cooling.	With Starch.			
0.5	1.0	100	30	Pale yellow	None	0.2282	0.2271	0.0011—
0.5	1.0	100	30	None	None	0.2283	0.2066	0.0017—

TABLE II.

0.5	0.5	120	50	None	None	0.2258	0.2235	0.0023—
0.5	0.5	100	50	Pale yellow	None	0.2252	0.2235	0.0017—
0.5	0.5	100	50	Pale yellow	None	0.2178	0.2163	0.0015—
0.5	0.5	100	50	Trace	None	0.2231	0.2231	0.0000
0.5	0.5	100	40	Trace	None	0.2261	0.2235	0.0026—

TABLE III.

0.5	0.5	100	50	Pale yellow	Faint	0.2268	0.2265	0.0003—
0.5	0.5	100	50	Pale yellow	Faint	0.2306	0.2300	0.0006—
0.5	0.5	100	50	Pale yellow	Faint	0.2272	0.2264	0.0008—

neutralisation, of a small amount of iodine chloride, which, in accordance with what is known of its modes of formation, might be formed by the oxidising effect of the antimonious and arsenic oxides upon the mixed acids. At all events, it is evident that if iodine chloride were present we should expect to note the phenomena which we do see; it would give, in small quantity, little or no colour to the liquid, would not show the starch reaction for free iodine in the acid solution, and would be destroyed with the formation hydrochloric and hydriodic acids by the addition of sulphurous acid to the still acid liquid, leaving the antimony unchanged and determinable iodometrically in alkaline solution after the exact oxidation of the excess of sulphurous acid by iodine in acid solution; on the other hand, it would act in alkaline solution like the free halogens, and tend to diminish the antimony indicated by titration. Whatever the real cause or causes of the deficiency may be, it appears, in the results of Table III., that the treatment with sulphurous acid affects the indications favourably. The mean error of three closely agreeing determinations is 0.0006 grm., and this is plainly within the limits of allowable variation in iodometric work with decinormal solutions.

It appears, therefore, that hydriodic acid may be made to serve satisfactorily as a substitute for the ferrous chloride of Fischer's original method, or for the ferrous sulphate of the modification of Classen and Ludwig, the determination of the residual antimony being perfectly practicable. The method of proceeding which we advocate is briefly summarised in the following statement:—To the solution of the oxides of arsenic and antimony, taken in amounts not exceeding 0.5 grm. of each, potassium iodide is to be added in a little more than the equivalent quantity, and enough strong hydrochloric acid to raise the entire volume of the solution to 100 c.m.^a Hydrochloric acid gas is passed into the liquid to saturation as well as during the distillation to follow, and the distillation is carried on until the volume of the liquid decreases to 50 c.m.^a or a little less. The liquid is cooled rapidly, treated first with an excess of sulphurous acid, and then with iodine to the exact oxidation of the former reagent; and, after the addition of 1 grm. of tartaric acid to every 0.2 grm. of antimonious oxide, the acid present is nearly neutralised with sodium hydrate, the neutralisation being completed by hydrogen sodium carbonate added in excess to an amount corresponding to 10 c.m.^a of the saturated solution for every 0.1 grm. of antimonious oxide present. Titration with decinormal iodine standardised against tartar emetic gives the antimony quickly and with a fair degree of accuracy. The whole process requires about an hour and a half for completion.

A New Washing-Bottle.—V. Hybinetto.—Referring to the description of a washing-bottle (*Zeit.*, xxx., p. 591) the author states that he has used such an apparatus for some years.

THE SEPARATION OF RESIN FROM FATTY ACIDS.

By J. ARTHUR WILSON.

THE detection of resin and its separation from fats and oils was at one time a very difficult problem to the analyst, and in many cases was impossible. Amongst many processes we have those of Henderson, Barfoed, and Gladding, the latter of which has found the greatest favour. It suffers from one very serious defect, however, and that is the correction for solubility of the fatty acids and silver salts in ether. This is a very variable factor, and, of course, is dependent on the nature of the fatty matter used in the fabrication of the soap. With small quantities of resin the error thus introduced may be as much as 20—30 per cent, but of course in soaps of high resin content—say 20 per cent—the error diminishes.

Mr. R. Williams (*Analyst*, vol. xv., p. 169) obtained very good results by the process; thus, in a soap which actually contained 30.0 per cent of resin, he obtained 30.7 per cent, but no mention is made as to whether the amount remaining in the lyes, after precipitation of the soap, was determined. As to the simple detection of resin, no doubt the best test is to boil the dry fat or fatty acids (10 drops) with 5 c.c. acetic anhydride, cool, and add 2 drops of pure sulphuric acid (1.84 specific gravity), when the reddish violet colour due to resin is easily observed, 1 per cent of which can thus be detected.

It seems that all the above processes must make way for the admirable process of Twitchell (*Analyst*, Oct., 1891), who found that whereas fatty acids are, as is well known, converted into neutral ethers on passing dry hydrochloric acid gas into their alcoholic solution, the acids constituting resin are not attacked. The process obviously may be either gravimetric or volumetric, but chemists will prefer the latter on account both of speed and accuracy. The description of the process is as follows:—2.5 to 3 grms. of the dried fatty and resin acids are dissolved in from 25—30 c.c. of perfectly absolute alcohol, and a current of dry hydrochloric acid gas passed in constantly. The flask containing the mixture must be kept cool by immersion in cold water. When the etherification is complete the ethers separate and the gas is no longer absorbed. The flask is removed, corked well, and allowed to stand half an hour. It is diluted with about 100 to 125 c.c. hot water, then cooled, transferred to a separatory funnel, and agitated with 75 c.c. of ether. The watery layer is removed, and the ethereal layer washed with cold water till neutral to delicate litmus solution (twice always is sufficient). The ethereal liquid is received in a flask, the separator washed out with about 50 c.c. of neutral spirit, and the whole titrated by standard alcoholic alkali, using phenolphthalein as indicator. The alkali should be standardised by an accurate solution of half normal HCl, and should be either one-fifth or one-half normal

according to the amount of resin in the fatty acids. Taking the mean combining weight of resin as 347, then the percentage is easily calculated; it is reported both on 100 of dry fatty matter and on 100 of soap.

Twitchell's test experiments are eminently satisfactory, and I have now pleasure in confirming them by my own tests:—

1. Sample of distilled fatty acids containing no resin, when treated as described, showed 0.7 per cent resin.
2. The above distilled fatty acids, to which were added common resin to the extent of 22.5 per cent, showed, when treated as above described, 23.3 per cent of resin, which, after deducting the 0.7 per cent found in No. 1, gives exactly 22.5 per cent, or the amount which was added.
3. Soap made from palm oil and other fats, but no resin, gave 0.8 per cent resin.
4. Another soap made from fatty matter of unknown origin, but no resin, gave 1.0 per cent resin. This, it should be observed, was of a dark colour, and evidently contained some altered or oxidised oily matter.
5. Soap which showed by Gladding's test 6 per cent of resin, gave 4.9 per cent by Twitchell's process.

The above results are all that may be desired, and I have now to show how the process may be still further shortened without any sacrifice of accuracy. This can be done by leaving out the washing and dissolving in alcohol direct. A few drops of methyl orange are then added and alkali till neutral to this indicator; phenolphthalein is then added, and the titration completed as before. The alkali required in the first case is for the neutralisation of the free hydrochloric acid, and is of course neglected. That required to neutralise phenolphthalein is of course due to the resin, and is calculated as such.

Tottenham Mills,
Oct. 6, 1891.

THE ESTIMATION OF COMBINED ALKALI IN SOAP.

By J. ARTHUR WILSON.

THE writer, who was the first to point out the error attendant on the use of the alcohol method of determining free caustic alkali in soap (CHEMICAL NEWS, vol. lix., p. 280; *Four. Soc. Chem. Industry*, vol. viii., p. 479), advised, when both free fat and free caustic alkali are present simultaneously, the adoption of the following method:—

Determine, firstly, the total alkali in the usual manner. Then determine the amount of alkali required to neutralise the isolated fatty and resin acids from a weighed quantity of the soap. Obviously the difference is the alkali present as hydrate, carbonate, or silicate of soda, &c. In the same paper above mentioned the following sentence occurs:—"Supposing palm, nut, or cocoanut oil to have been used in the fabrication of the soap, the determination of the Na_2O required to neutralise the fatty acids becomes inaccurate, owing to the solubility of the lower fatty acids; hence another complication arises. The error, of course, may be of greater or less extent, according to the nature of the fatty matter of the soap." Fortunately, this error can be completely excluded by operating in a very simple manner as follows:—

1. The alkali, in all forms, is determined by titration with standard acid in the usual manner.
2. Another weighed quantity of the soap is decomposed in an Erlenmeyer flask with a slight excess of dilute H_2SO_4 , and the flask kept on the water-bath till the fatty acids separate quite clear. The flask is then placed in ice water to cool, and then filtered. The fatty acids are washed three times successively with 250 c.c. of boiling water and allowed to cool each time and filtered. The

united filtrates are diluted to 1 litre, and 500 c.c. placed in a clear white beaker and tinted with methyl orange; N/10 alkali is then dropped in till the liquid acquires the usual colour, after which a little phenolphthalein is added, and the addition of standard alkali continued till a permanent pink is established. The number of c.c. used in the latter titration are due to the soluble acids, and are calculated to caprylic acid. The fatty acids in the flask, and any little on the filter, are dried and weighed, and then dissolved in alcohol, and titrated with N/2 alcoholic alkali. The alkali so used, together with that required for neutralisation of the soluble acids, and deducted from the total alkali, gives the alkali existing in other forms than as soap.

Of course, if desired, the soap may be decomposed with standard H_2SO_4 , and the alkali required to neutralise the methyl orange noted, which, deducted from the total acid used, would give the acid equivalent to the alkali existing in all forms. In this manner we get—

Total alkali	..	..	..
Combined alkali	..	..	..
Insoluble fatty acids	..		
Soluble	"	"	..

The following examples illustrate the method:—

No. 1.—*Soap from Cocoanut Oil and other Fats (Highly Watered). Total Alkali by Titration, 2.06 per Cent Na_2O .*

Weight of soap taken	..	..	17.145 grms.
Weight of insoluble fat acids	..	2.29	" = 13.35%
C.c. of N/2 alkali to neutralise	..	16.1	" = 8.05 normal.

C.c. of N/10 alkali to neutralise soluble acids 4.2 " = 0.42 normal

C.c. of N/10 alkali to neutralise soluble acids 4.2 = 0.42 normal = 0.36 per cent soluble acids (= caprylic).

Total alkali used for both soluble and insoluble fatty acids, c.c., = 8.47 normal.

$$\frac{8.47 \times 0.031 \times 100}{17.145} = 1.53 \text{ per cent combined alkali.}$$

	Per cent.
Total alkali (Na_2O)	2.06
Combined alkali (Na_2O)	1.53
Uncombined	0.53
Soluble fatty acids	0.36 = caprylic.
Insoluble	13.35
Total fatty acids	13.71

No. 2.—*French Scouring Soap. Total Alkali by Titration, 7.037 per Cent.*

Weight of soap taken	..	..	5.889 grms.
Weight of insoluble fatty acids	..	2.005	" = 34.06%
C.c. of N/2 alkali to neutralise	..	18.05	" = 9.025 normal.

C.c. of N/10 alkali to neutralise soluble acids, 10.7 = 1.07 normal = 2.6 per cent caprylic acid.

Total alkali used for both soluble and insoluble acids = 10.1 c.c. normal = 20.2 N/2.

$$\frac{20.2 \times 0.0155 \times 100}{5.889} = 5.32 \text{ per cent combined alkali.}$$

	Per cent.
Total alkali (Na_2O)	7.037
Combined alkali	5.32
Uncombined	1.717
Insoluble fatty acids	34.06
Soluble	2.6 = caprylic.
Total	36.6

Tottenham Mills, October

SEPARATION AND DETERMINATION
OF TELLURIUM.

By E. DONATH.

IN the determination of tellurium by the older method generally followed—precipitation from a hydrochloric solution with sulphurous acid in heat—a complete separation is effected, but the process is very tedious. After heating for some hours, and on addition of sulphurous acid in excess, slight separations of tellurium are still obtained in the concentrated filtrates. H. Rose's statement, that the separation by means of sulphurous acid is not more tedious than that by means of sodium thiosulphate, is confirmed by Donath.

In precipitating tellurium by glucose in a boiling alkaline solution, as proposed by Stolba and used by Lad. Kästner, the separation is complete and soon effected. The deposit of tellurium can be either weighed on a tared filter or dissolved off the filter by dropping upon it nitric acid, moderately diluted and heated (2 parts nitric acid and 1 part water, with a few drops of sulphuric acid). The solution is then concentrated in a small porcelain capsule, and the residue, after gentle ignition, is weighed as tellurous acid, TeO_2 .

The author's proposed method—precipitation by stannous chloride or an alkaline solution of stannous oxide—led to no satisfactory results. The separation in an acid solution by means of hydrosulphurous acid was quite successful. A solution of this acid can be easily and rapidly prepared by digesting zinc clippings with aqueous sulphurous acid, or by covering the clippings with a concentrated solution of sodium bisulphite and cautiously acidulating the solution with a little hydrochloric acid. The deep yellow solution thus obtained, which must be filtered before using, precipitates tellurium at once in the cold, and, if not too dilute, in the form of flocks which subside readily. If the hydrosulphurous acid is not decomposed, the tellurium is separated as such; if the liquid is heated, and even otherwise, in consequence of the almost inevitable decomposition of the hydrosulphurous acid, the tellurium subsides mixed with tellurium sulphide, and the liquid becomes opalescent in consequence of finely suspended sulphur. In concentrated hydrochloric solutions and with a suitable excess of hydrosulphurous acid the precipitation is complete after heating for fifteen minutes. The washed precipitate is rinsed through the perforated filter into a tared capsule, a little concentrated acid is added, the solution is evaporated down, and the residue, after slight ignition, is weighed as tellurous acid.

This rapid process has the disadvantage that it is impracticable in presence of many metallic oxides. Thus, salts of bismuth are precipitated by hydrosulphurous acid at common temperatures, and on heating the liquid other metals of the H_2S group are precipitated by the hydrosulphurous acid formed on the decomposition of the hydrosulphurous acid.

On using a pure solution of an alkaline tellurite, concordant and accurate results were obtained by precipitation with glucose in an alkaline solution, and with hydrosulphurous acid in an acid solution.

The opening up of products, or minerals containing tellurium, and its separation from accompanying elements, were attempted by the author in various manners. After many fruitless experiments, he succeeded in developing a method which meets all fair demands as regards accuracy and despatch.

About 3–4 grms. of the very finely pulverised sample are gradually oxidised in a porcelain capsule with a minimum of concentrated nitric acid, and the thick pasty mass is heated until all excess of nitric acid is eliminated. The temperature must not be raised high enough to decompose the less stable iron, copper, and bismuth nitrites. In this case, there would be formed from the tellurous acid, telluric acid; and, subsequently, very sparingly

soluble tellurates, the formation of which must be avoided. The dry mass obtained is ground finely in the capsule with an agate pestle, and moistened with concentrated soda-lye, which becomes strongly heated by the transformation of the nitrates. After digestion for thirty minutes, a little more soda-lye and a corresponding quantity of water are added, the liquid is filtered off, and the tellurium is precipitated in the filtrate by boiling for at most twenty minutes with a pure solution of glucose, and it is either determined as such or as tellurous acid.—*Zeit. Anal. Chemis.*

DETECTION OF ADULTERATIONS OF BASIC
SLAGS.

By DR. MORGAN.

IN the Agricultural Section of the German Congress of Naturalists and Physicians the author pointed out various methods for the qualitative detection of adulterations in basic slag. The loss on ignition is important. If the sample is genuine there is no loss. If it amounts to $\frac{1}{2}$ –1 per cent, the sample is almost always adulterated. The determination of the specific gravity also gives a clue, especially in the case of sophistication with redonda phosphate. The author does not use for this determination a solution of mercuric potassium iodide, but bromoform (specific gravity = 2.9).

Treatment with dilute soda-lye separates redonda phosphate and basic slag. If there is an impurity of redonda phosphate a very copious precipitate is produced.

If the coarsely ground sample is examined yellow particles are found if redonda phosphate is present, but not in case of a pure basic slag.

The best method for a quantitative determination is that of Jantsch and Schucht. The P_2O_5 of basic slag is perfectly soluble in 5 per cent citric acid, but not that of redonda phosphate.

"Taffin" slag behaves like basic slag, but it remains suspended in bromoform. Dr. Loges, of Posen, mentioned a new spurious material said to be of English origin. The small sample which he had obtained contained 4 per cent caustic lime, 6.4 per cent calcium carbonate, as well as calcium fluoride. It is probably sophisticated with Welsch phosphate.—*Chemiker Zeitung.*

DETECTION OF FORMLESS FERMENTS
AND POISONS IN BLOOD.

PROF. R. KOBERT.

BOTH the physiological and the chemico-legal demonstration of unstable poisons in blood encounter difficulties depending mainly on the fact that the colouring-matter of the blood (if the red globules are dissolved by putrefaction, morbid processes, or improper treatment such as the addition of water), forms a tarry mass which it is difficult to treat chemically and which is perfectly useless for physiological experiments. The removal of this tarry colouring-matter is generally effected by plentiful dilution and boiling with acetic acid, or precipitation with alcohol, with potassium ferrocyanide and acetic acid, or with uranium nitrate.

In all these cases the serum albumen present in the blood along with the blood-pigment as well as all albumenoid enzymes and toxalbumens are simultaneously precipitated, and thus the detection and the isolation of the enzymes and toxalbumens is rendered impossible. But if we had an agent which would throw down the colouring-matter of the blood, leaving all other substances in solution, and chemically unaltered, we should have made

an important step towards the isolation and detection of the enzymes and toxalbumens.

Zinc-powder may be regarded as such a precipitant for hæmoglobine. In forensic chemistry which is generally concerned with stale, offensive blood, this agent has the advantage that it renders the specimen almost inodorous even if several weeks old. The completeness of the precipitation is not interfered with by the age of the blood. The following conditions are essential for successful precipitation:—

1. In quite recent blood, freshly drawn from normal men or other animals, which is always alkaline, the alkalinity must be neutralised before the addition of the zinc powder. The same holds good of the blood of dead bodies a week old in which ammonia has been formed. On exposure to the air, or remaining in the body, the normal alkalinity of the blood is lost within 1 to 2 days. Diseases—especially fevers—often reduce the alkalinity before death to such a degree that the zinc may be added directly.

2. The blood must be free from methæmoglobine. If this substance is present the blood is allowed to remain in an open vessel without dilution or shaking until the last trace of methæmoglobine has disappeared. It is known that this disappearance often ensues within 24 hours, whether in the corpse or in jars, even when the original quantity of methæmoglobine was very considerable.

3. The blood must be diluted with at least 3 to 5 volumes of water.

4. The zinc-powder must be as pure as possible, containing nothing but zinc and zinc oxide.

5. The quantity of the zinc-powder must be equal to a quarter or a half of the original weight of the blood.

6. The mixture must be energetically shaken for a considerable time.

If these conditions are observed a complete separation of the colouring-matter of the blood is almost always effected, so that even on washing the precipitate with much water in the filter-press or in the filter-pump nothing returns into solution. The yellowish brown colouring-matter contained in the serum of some kinds of blood is not thrown down, but remains in the filtrate. Distinctly recognisable quantities of zinc are to be found in the filtrate only if compounds of organic acids were present in the blood. Otherwise mere traces of zinc exist as zinc albuminate, in smaller proportions the more the zinc powder is free from zinc oxide. As the deposit—a solid, reddish-brown, bulky mass,—retains no organic poisons except traces of hydrocyanic acid and carbon monoxide, we have in the filtrate all the glycosides, alkaloids, ptomaines, toxalbumens, enzymes, amides, &c.; in short, the examination of the filtrate is exclusively important for forensic chemistry. Concerning the solid residue we need merely remark that the hydrocyanic acid may be removed from it by extraction with alcohol and carbon monoxide by exhaustion in the air-pump.

The filtrate is incomparably more suitable than the original blood as well for the chemical as for the physiological detection of poisons. If its action upon animals is to be examined it is only requisite to shake up a portion with a drop of solution of sodium sulphide, and to filter off the precipitate of zinc sulphide. If the proportions are duly adjusted the liquid, free from zinc and sodium sulphide, can be injected subcutaneously into a mouse or into the circulatory system of a kitten. However, the filtrate can often be applied without the elimination of the zinc. The bacteria which swarm in putrid blood are almost entirely left behind in the residue. Where an absolute determination of bacteria is required the filtrate may be again passed through a Chamberland filter and thus the last residues of the germs may be removed. If the animal experimented upon exhibits grave phenomena of poisoning, a second portion of the original filtrate is mixed with a drop of solution of potassium ferrocyanide and a little acetic acid, the precipitate, which includes all

the zinc and the albumenoids, is filtered, the filtrate is neutralised and injected into a second animal. If this animal, in contradistinction to the former, exhibits no phenomena of poisoning, the symptoms observed in the former subject must have been occasioned by an albumenoid poison, as in such dilute liquids other poisons are not precipitated by potassium ferrocyanide, or at most a portion of strychnine, which can be easily detected in the precipitate.

The isolation of the poisonous albumenoid substance can be undertaken only in the main portion of the original filtrate, either by treatment with alcohol in the ordinary manner or by "salting out" with ammonium sulphate. In those toxalbumens, however, which do not admit of the above mentioned methods of precipitation, *e.g.*, those of venomous spiders, a more complete isolation of the poison is not yet practicable.

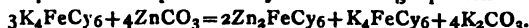
If the second experimental animal does not remain in health, but is taken ill like the first, we have a proof that the poison in question does not belong to the albumens,—at least not to those precipitable by ordinary means. The entire filtrate is then freed from albumen and the limpid filtrate is examined for other poisons by Dragendorff's method.—*Chemiker Zeitung*.

NEW METHOD FOR THE EXAMINATION OF FERROCYANIDES, FOR DETERMINING THE VALUE OF PRUSSIANE MELT, AND FOR ESTIMATING THE FERROCYANIDE IN SPENT LAMING'S MASS.

By R. ZALOZIECKI.

THE method is founded on the fact that the ferrocyanides in a solution of potassium or sodium ferrocyanide may be completely precipitated in the form of double ferrocyanides of zinc and alkali by an addition of zinc carbonate and the introduction of a current of carbonic acid gas. The equivalent quantity of potassium or sodium separated by the zinc from the ferrocyanides is transformed into the corresponding potassium or sodium carbonate, and the quantity of the ferrocyanide originally present may be found by an alkalimetric determination of the alkaline carbonate formed.

According to the experiments of the author, 3 mols. potassium ferrocyanide yield on decomposition 2 mols. zinc ferrocyanide, whilst 1 mol. potassium ferrocyanide remains undecomposed. The double salt therefore corresponds to the formula $2\text{Zn}_2\text{FeCy}_6 + \text{K}_4\text{Cy}_6$, and the decomposition is represented by the following equation—



The reaction always takes place uniformly in heat, and even in the cold the transformation of potassium ferrocyanide is effected according to the above equation. A solution of sodium ferrocyanide behaves differently, since in the cold there is formed a double salt poorer in zinc, though in heat the same decomposition takes place as with potassium ferrocyanide. It is therefore always necessary to operate in heat.

The zinc carbonate to be used in the process is obtained by precipitating in heat a solution of zinc sulphate with sodium carbonate; the basic carbonate thus obtained settles rapidly, and may be easily washed. It is convenient to weigh approximately whilst in the moist state the basic zinc carbonate obtained from a known quantity of zinc sulphate, and preserve it in a closed glass jar. The author generally uses in his experiments 20 grms. moist zinc carbonate, corresponding to 2.25 grms. zinc. Such an excess does not affect the results, but the decomposition may be produced completely by a much smaller quantity of zinc.

In a determination of ferrocyanide the solution of the salt is mixed in a small flask with a known quantity of zinc carbonate, and carbonic acid is passed into the heated solution for from half to one hour. The treatment with carbonic acid is continued until the original decided yellow colour of the solution has disappeared, or until the addition of a ferric salt to a portion of the clear liquid no longer gives a blue precipitate. When cold it is put into a measuring flask containing 250 c.c., filled up to the mark, and filtered through a dry filter into a dry flask, wherein 50 c.c. of the filtrate are titrated with sulphuric acid of known strength as indicator. According to the above equation the quantity of the ferrocyanide can be calculated from the potassium or sodium carbonate thus determined, as four equivalents of potassium or sodium carbonate represent three equivalents of ferrocyanide.

The author observed that the presence of large quantities of alkaline sulphates or chlorides lead to the formation of a compound richer in zinc. This effect is annulled if at the same time there is present an excess of alkaline carbonate. In examining the salts of prussiate melts the presence of sulphates must be taken into consideration, and in case the sulphates are present in considerable quantity a known excess of potassium or sodium carbonate must be added prior to the introduction of the zinc carbonate; otherwise the results will be too high.

For the examination of prussiate melts the author gives the following directions:—10 grms. of melt are dissolved in 100 c.c. of water, the volume of the insoluble residue being taken into consideration. In 25 c.c. of the solution the alkalinity is determined with normal acid and methyl orange: 50 c.c. of the solution are treated, as described above, with 10 grms. moist zinc carbonate, carbonic acid is introduced for half an hour into the hot solution, which when cold is placed in a 100 c.c. flask, and filled up to the mark; 50 c.c. of this solution are titrated with decinormal acid after the number of c.c. acid required for the alkalinity of the mark have been added.

If, in the determination of the alkalinity in the coloured solution of the melt, the change of colour is difficult to recognise, the solution can be exactly neutralised with dilute sulphuric acid, and, prior to the decomposition with zinc carbonate, 20 c.c. of a normal solution of potassium carbonate. There is no difficulty in titrating back, as the liquid is colourless after the decomposition. If the acid is so standardised that 1 c.c. corresponds to 0.001 grm. potassium carbonate, the c.c. of the acid consumed in neutralising the potassium carbonate formed, multiplied by 0.8, give the per cents of anhydrous potassium ferrocyanide, and if multiplied by 0.92 the percentage of hydrous ferrocyanide in the original melt.

Sulphocyanides, if present, do not affect the result. Potassium sulphide is indeed converted into zinc sulphide and potassium carbonate, but this decomposition has no effect, as the potassium sulphide present is included in the result on determining the total alkalinity with methyl orange as indicator.

The method is applicable also in determining the ferrocyanide in spent "mass" from the gas purifiers (Laming's mass).

Zaloziecki proceeds as follows:—20 grms. of the mass, in a state of fine division, are gently heated on the water-bath for fifteen minutes with 20 c.c. 10 per cent potassa lye and a little water in a 100 c.c. flask. When the entire quantity of the ferrocyanide present is thus dissolved it is let cool, and the flask is filled up to the mark: 50 c.c. of the clear solution (or, more correctly, 45 c.c. if measured with a burette, as 20 grms. of the mass take up a volume of 10 c.c.), corresponding to 10 grms. of the sample, are boiled in a 100 c.c. flask over an open fire until the ammonia is entirely expelled, and it is then accurately neutralised with dilute acid. To facilitate the neutralisation a few drops of solution of phenolphthalein may be added, and the acid dropped in from a burette until the red colour disappears. On neutralisation

the sulphur separates out and the liquid becomes turbid, but this does not interfere with the further determination. The expulsion of the ammonia may also be effected by the addition of milk of lime, and the lime may next be removed by the solution of potassa, which renders the liquid clear. The solution thus prepared, in which all the ferrocyanogen is combined with potassium, cannot be at once submitted to treatment with zinc carbonate and carbonic acid, as potassium sulphate (or chloride) is present in quantity, and would interfere with the reaction. He therefore first adds to the solution 20 c.c. of normal potassium carbonate, and then undertakes the decomposition in the manner described above, adding 5 grms. moist zinc oxide, and then passing carbonic acid for half an hour through the hot solution. When the reaction is completed, and the liquid is cooled, the flask is filled up to the mark, and one-half of the liquid—representing 5 grms. of the mass—is titrated with decinormal acid and methyl orange. The quantity of normal acid equivalent to the normal potassium carbonate added (10 c.c.) is either added at the outset or deducted from the total sum of c.c. of acid consumed.

If the acid has been so standardised that 1 c.c. represents 0.001 grm. potassium carbonate, the c.c. of acid consumed in titrating back, if multiplied by the coefficient 0.46, will give the percentage of crystalline ferrocyanide existing in the purifying mass.—*Zeitschrift Analyt. Chem.*, vol. xxx., 484.

PROPERTIES OF PRECIPITATES, &c.

By E. WALLER, Ph.D.

ONE division of Fresenius's book on "Quantitative Analysis" treats of "forms," in which are given the properties of the various forms in which substances are separated for the purpose of weighing and determination.

It has seemed to the writer that those properties might be described in a manner more convenient for reference, and also that there might be added the properties of various precipitates, &c., which are used in analytical work for purposes of separation. Of course only those properties are considered which have a bearing on the usual manipulation of the different substances. For convenience the information has been grouped under the heads—

"Remarks" (*Rem.*), giving points not properly belonging under any of the succeeding heads.

Conditions (*Cond.*), referring to the character of the solutions in which the separation can be made.

Solubilities (*Sol.*), under which the influences of different solvents which may be used in ordinary work are considered.*

Contaminants (*Contam.*), which is restricted to those substances only which would not be expected to precipitate if alone under the conditions obtained.

Ignition (*Ign.*), or the behaviour of the compounds designated on heating to a high heat in the way usually pursued with most of them. Under this head it is also necessary to consider the effect of ignition in contact with filter paper or other carbonaceous substances indicated for brevity as "C."

A Table is given which is intended to indicate at a glance the precipitates, &c., used, and the forms in which they are weighed in case that is the object in view. Of course the forms designated as for weighing can also be used for purposes of separation.

* The terms "soluble" and "insoluble," as used in text-books of analytical chemistry, are usually misunderstood by students. The terms are used in a relative—not in an absolute—sense, e.g., when a precipitate is said to be "insoluble," the meaning usually is that under ordinary conditions of work, with a moderate bulk of solution, &c., the degree of solubility is so small that no material error is involved by regarding the separation as complete.

Element, &c.	Purpose.	Obtained, or precipitated as—	Prepared for weighing by—	Weighed as—
NH ₄	Weighing.	(NH ₄) ₂ PtCl ₆ .	Drying or ignition.	(NH ₄) ₂ PtCl ₆ or Pt.
K	"	K ₂ PtCl ₆ .	"	K ₂ PtCl ₆ or Pt.
	"	KCl.	Ignition.	KCl.
	"	K ₂ SO ₄ .	"	K ₂ SO ₄ .
Na	"	NaCl.	"	NaCl.
	"	Na ₂ SO ₄ .	"	Na ₂ SO ₄ .
Ca	"	CaC ₂ O ₄ .	{	CaSO ₄ .
	"	CaCO ₃ .		CaCO ₃ .
	"	CaO.		CaO.
Mg	Separation.	MgNH ₄ PO ₄ .	"	Mg ₂ P ₂ O ₇ .
	Weighing.	Mg(OH) ₂ .	"	
Ba	Separation.	BaSO ₄ .	"	BaSO ₄ .
	Weighing.	BaCO ₃ .	"	
Fe	Weighing.	Fe ₂ (OH) ₆ .	"	Fe ₂ O ₃ .
	Separation.	Fe(OH) ₃ (C ₂ H ₃ O ₂) ₆ ·n.	"	
Al	Weighing.	Al ₂ (OH) ₆ .	"	Al ₂ O ₃ .
	"	Al ₂ (PO ₄) ₃ .	"	Al ₂ (PO ₄) ₃ .
	Separation.	Al ₂ (OH) ₃ (C ₂ H ₃ O ₂) ₆ ·n.	"	
Cr	Weighing.	Cr ₂ (OH) ₆ .	"	Cr ₂ O ₃ .
Ti	"	H ₂ TiO ₃ .	"	TiO ₂ .
	Separation.	Na ₂ TiO ₃ .	"	
Zn	Weighing.	2ZnCO ₃ ·3Zn(OH) ₂ .	" or drying.	ZnO.
	"	ZnNH ₄ PO ₄ .	"	Zn ₂ P ₂ O ₇ or ZnNH ₄ PO ₄ .
	Separation.	ZnS·H ₂ O.	"	
Mn	Weighing.	2MnCO ₃ ·H ₂ O.	Ignition.	Mn ₂ O ₃ .
	"	MnNH ₄ PO ₄ .	"	Mn ₂ P ₂ O ₇ .
	Separation.	MnO ₂ .	"	
Ni	Weighing.	Ni (electro).	Drying.	Ni.
	"	Ni(OH) ₂ .	{	NiO.
	"	Ni ₂ (OH) ₆ .		
	Separation.	NiS·H ₂ O.	"	
Co	Weighing.	6KNO ₃ ·Co ₂ (NO ₂) ₆ .	Ignition.	3K ₂ SO ₄ + 2CoSO ₄ .
	Separation.	CoS·H ₂ O.	"	
Cu	Weighing.	Cu (electro).	Drying.	Cu.
	"	Cu(OH) ₂ .	Ignition.	CuO.
	"	CuS.	"	Cu ₂ S.
Pb	"	PbSO ₄ .	"	PbSO ₄ .
	"	PbCrO ₄ .	Drying.	
	Separation.	PbS.	"	
Ag	Weighing.	AgCl.	Ignition.	AgCl.
As	"	As ₂ S ₃ .	Drying.	As ₂ S ₃ .
	"	MgNH ₄ AsO ₄ .	Ignition.	Mg ₂ As ₂ O ₇ .
Sb	"	Sb ₂ S ₃ .	" or drying.	Sb ₂ O ₃ or Sb ₂ S ₃ .
Sn	"	H ₁₀ Sn ₅ O ₁₅ .	"	SnO ₂ .
	"	SnS ₂ .	"	
S ₂ SO ₃ S ₂ O ₃ SO ₃ , &c... ..	"	BaSO ₄ .	"	BaSO ₄ .
P ₂ P ₂ O ₅ , &c.	"	MgNH ₄ PO ₄ .	"	Mg ₂ P ₂ O ₇ .
	Separation.	12MoO ₃ (NH ₄) ₃ PO ₄ +	"	
C, CO ₂ , &c.	Weighing.	{ Na ₂ CO ₃ , K ₂ CO ₃ , &c., or	Absorption.	{ Na ₂ CO ₃ , K ₂ CO ₃ , &c., or
Si and SiO ₂	"	{ Na ₂ CO ₃ + CaCO ₃ ·BaCO ₃ }	Ignition.	{ Na ₂ CO ₃ + CaCO ₃ ·BaSO ₄ .
Cl	"	xH ₂ OSiO ₂ .	"	SiO ₂ .
N and HNO ₃	Measuring.	AgCl.	"	AgCl.
	Titration.	N or NO.	"	
	Weighing.	NH ₃ .	"	
		(NH ₄) ₂ PtCl ₆ .	"	(NH ₄)PtCl ₆ or Pt.

$(\text{NH}_4)_2\text{PtCl}_6$.

Rem.—Precipitant, PtCl_4 .

Yellow, perceptibly crystalline if formed slowly. Sometimes it is dissolved from the paper by hot water into a weighed capsule, and the solution evaporated, thus avoiding the uncertainties involved in the use of weighed filters.

Cond.—Solution should contain only chlorides. Sodium salts only permissible. Solution should be cold, slightly acid, consisting chiefly of strong alcohol; an excess of PtCl_4 should be present.

Sol.—Somewhat soluble in cold, more so in hot, water. Fairly insoluble in strong alcohol, though more soluble than the corresponding potassium compound. Solubility in alcohol diminished by addition of ether. Its solubility also increases more rapidly by a rise in temperature or the dilution of the alcohol. Solubility increased by acid (HCl) or by alkali, diminished by PtCl_4 or Na_2PtCl_6 .

Contam.— NaCl , which is not very soluble in alcohol. If sufficient PtCl_4 has been added to form Na_2PtCl_6 , the amount of contamination is small. The Na_2PtCl_6 crystals are more strongly coloured and different in shape (needle shaped), so that they can be readily detected. Can be removed by a short digestion with cold alcohol.

Ign.—Decomposed, leaving spongy platinum. Unless the heat is slowly raised some Pt may be volatilised with the products of decomposition.

KCl.

Rem.—Obtained by evaporation of the solution and gentle ignition. Frequently, when in admixture with NaCl , the sum of the chlorides is thus obtained, and the KCl determined by PtCl_4 , the NaCl calculated, or the chlorine is determined and the proportions calculated. Salts containing K combined with acids capable of expulsion by HCl , may be evaporated with excess of HCl .

Cond.—Solution should contain only chloride or salt convertible into chloride by evaporation with HCl . Ammonia salts and such others as may be expelled by evaporation and gentle ignition may be present.

Sol.—Soluble in water, less so in alcohol or strong HCl .

Contam.— NaCl , see under remarks. If the solution has been long exposed to the air of the laboratory, it usually contains some organic dust, which carbonises by ignition, requiring filtering and re-evaporation.

Ign.—Decrepitates somewhat unless dried for some time. Fuses at a low red heat, and volatilises at temperatures a little higher, a small amount of caustic alkali being usually formed at the same time.

 K_2SO_4 .

Rem.—Obtained by evaporation of the solution, or by adding H_2SO_4 to solutions containing combinations with volatile acids (chloride, nitrate, acetate, &c.), evaporating, and igniting. In cases of admixture with Na salts, processes similar to those indicated under KCl may be used.

Cond.—Salts forming non-volatile sulphates, or containing non-volatile acids (H_3PO_4 , &c.) should be absent.

Sol.—Moderately soluble in water; much less so in alcohol.

Contam.— Na_2SO_4 or other non-volatile sulphates.

Ign.—Practically non-volatile in the heat of an ordinary Bunsen burner if the heat is not unnecessarily prolonged. Where the solution has contained an excess of H_2SO_4 , some undecomposed KHSO_4 always remains, which can be best decomposed, or converted into K_2SO_4 by heating with a few lumps of solid ammonium carbonate. Ignited with C, K_2S may be formed. The conditions usually obtained, however, do not afford this result.

(To be continued.)

Modification of the Spectroscope.—P. Schottländer (*Zeit. für Instrum. Kunde*).—The object is to determine the coefficients of extinction of absorbent bodies.

NOTICES OF BOOKS.

A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali with the Collateral Branches. By GEORGE LUNGE, Ph.D., Professor of Technical Chemistry at the Federal Polytechnic School, Zurich (formerly Manager of the Tyne Alkali Works, South Shields). Second Edition, Revised and Enlarged. Vol. I.—Sulphuric Acid. London: Gurney and Jackson. 8vo., pp. 940.

(SECOND NOTICE.)

THE author naturally does not overlook the nuisance arising from the escape of sulphurous acid, but he reminds his readers that chemical works are not the sole offenders in this respect, as this acid occurs in very large quantity in all coal smoke, and that the most perfect smoke combustion cannot do away with this. He shows that the vapours escaping from the high chimney shafts of factories are less hurtful than those from brick-kilns, coke-ovens, &c.

Metallic sulphides other than pure pyrites are often not good materials for the manufacture of sulphuric acid. According to Bode an admixture of 18–20 per cent of galena renders pyrites unfit for burning. The manufacture of nitric acid is fully described, with figures showing proposed modifications of the apparatus.

It is remarked that some manufacturers substitute for a part of the nitre used the waste acid from the production of nitrobenzene, nitroglycerin, &c. The author gives the caution that in this case all drops of oily matter must be carefully excluded.

When speaking of the injurious action of sulphur dioxide on animal and vegetable life the author notes some prevailing errors. Hirt has stated that 1–3 per cent SO_2 may be breathed without danger to health. Ogata, on the contrary (*Archiv. für Hygiene*), as here quoted, found experimentally that 0.04 per cent SO_2 causes difficulty of breathing in a few hours, and that he could not take a single full breath in air containing 0.05 per cent SO_2 . But the influence of acid vapours upon cattle, trees, and even upon the soil, has been grossly exaggerated.

The bleaching action of sulphurous acid has not, according to the author, been fully explained.

The occurrence of free sulphuric acid in certain animal secretions is mentioned as a curious fact. The saliva of *Dolium galea* contains 2.47 per cent sulphuric acid and 0.4 per cent hydrochloric acid both in the free state.

Whilst speaking of the specific gravity of "rectified oil of vitriol," called O.V., or sometimes D.O.V., the author refers to the inaccuracy of ordinary hydrometers. He remarks, however, "Still, it must be conceded that in England at least there is a possibility of making the hydrometers all alike, the basis of Twaddell's system being a plain and unmistakable one, as every degree is equal to a difference of 0.005. But matters are far worse on the Continent and in America, where Baumé's hydrometer is almost universally used. Unfortunately the degrees of this instrument, as stated by various authorities, answer to very different specific gravities, and those of the instruments found in trade often show even far greater deviations." The rational hydrometer on Baumé's system is graduated according to the formula—

$$d = \frac{144.3}{144.3 - n},$$

where d stands for any given specific gravity, and n for the degree Baumé corresponding. Another modification devised by Gerlach is also sometimes used on the Continent, whilst American manufacturers have adopted a third scale. If a liquid is found to mark 66° B., its specific gravity may, according to the scale adopted, be 1.842, 1.817, or 1.835!

As regards the specific gravities of mixtures of sulphuric

acid and water, the author uses the values determined last year by himself and Isler. For those of Bineau and Kolb the reader is referred to the former edition. Those of Ure and Dalton, and still more the tables of Vauquelin and D'Arcet, which, though totally incorrect, are still used in the south of France, are not quoted.

The experiments here given bearing on the behaviour of different mixtures of cast-iron with sulphuric acid are of great importance. The different qualities of cast-iron are equally resistant against acid of 168° Tw. and against weaker acids at 20° and 100°. Scotch pig and mixtures in which it is present are most attacked.

Both cast- and wrought-iron resist monohydrated sulphuric acid better than copper or lead.

The behaviour of lead, pure and alloyed, with sulphuric acid, is still open to doubt. The author's own experiments given in the appendix (p. 892) show that pure, soft lead is less attacked than the so-called "hard lead" containing 1·8 per cent of antimony. Glover (CHEMICAL NEWS, vol. xiv., p. 105) obtained corresponding results, whilst Calvert and Johnson, and subsequently Mallard and Hasenclever, find that lead is all the more acted upon the purer it is.

The section on the behaviour of sulphurous and sulphuric acid with the nitrogen oxides is very elaborate and of thorough practical value.

As a standard acid the author recommends hydrochloric acid. Oxalic acid, though extensively used, has, he considers, great drawbacks. It is extremely difficult to prepare in the pure and dry state without losing some of its crystalline water; it does not keep in weak solutions, and it cannot be employed with methyl orange, which he prefers as an indicator.

Among the impurities encountered in sulphuric acid a prominent place is of course due to arsenic. Here Selmi is quoted for the statement that arsenic may be detected in acid, which does not react with the Marsh test by diluting 1000 grms. of the sample with 300 grms. of water, adding some lead chloride, distilling and testing the first portions of the distillate with sulphuretted hydrogen.

For the analysis of nitrous vitriol the author uses a special modification of the permanganate process. The estimation of nitrous acid by means of aniline, which is converted into a diazobenzol salt, the end of the reaction being shown by potassium iodide. It offers no advantages as compared with the permanganate process, which is simpler.

For determining the total nitrogen acids in sulphuric acid the author recommends Walter Gram's process, for which he has constructed a special instrument, the "nitrometer," which is here figured. Since the publication of his paper, Campbell, Davis, and possibly others have all designed nitrometers which the author, however, considers less satisfactory than his own instrument. As the nitrometer, however, requires reference to certain tables, he has constructed another instrument, the gas-volumeter, which dispenses with the use of tables.

With chapter 4 the author enters upon the actual manufacture of sulphuric acid. He describes and figures in the first place the burners for brimstone now, of course, comparatively little used. Next follow the appliances for burning pyrites, beginning with the ore-breaker of Blake, as improved by Broadbent and Son, of Stalybridge, and those of Motte, Durand, and Chaptal Vapart, &c.

The pyrites-burners for lumps are exhaustively treated of, followed by the kilns for smalls. The original plan of working up smalls with clay into the form of balls involves so much inconvenience that it has been abandoned almost everywhere in favour of the shelf-kilns of Malétra, Schaffner, and others.

The various attempts to construct chambers of materials other than lead, or to dispense with them altogether, have proved unsuccessful. Their construction, arrangement, and dimensions are made the subject of elaborate consideration.

As regards the supply of nitric acid to the chambers,

there is a choice between the introduction of solid nitre, as most usual in Britain, of liquid acid, preferably running it along with the nitrous vitriol through the Glover tower, and of an aqueous solution of nitrate.

The respective advantages of the solid and the liquid form are fully weighed. Dr. Lunge's decision is distinctly in favour of the use of liquid acid.

Passing over the carefully written sections on the supply of steam and of air we come to the question of the optimum strength of chamber acid. In England strengths of 120°—130° Tw. are adhered to, whilst on the Continent 113° Tw. is rarely exceeded, and in America 112°—116°. The author awards the preference to the weaker acid.

The experiments of H. A. Smith ("Chemistry of the Sulphuric Acid Manufacture") are pronounced quite unsatisfactory. As regards the Glover tower the author's conclusion, drawn from the observation of many of the best alkali works—English, French, and German,—is distinctly favourable. So far from wasting nitre it has reduced the consumption of nitre and "forms an essential part of every well-arranged sulphuric acid works."

The drawbacks of the Glover tower are contamination of the acid with iron and alumina. Hence it cannot well be concentrated in platinum vessels.

Anent the formation of sulphuric acid the author discusses the theories of Clement and Désormes, of Davy, Berzelius, Peligot, R. Weber, Winkler, Raschig, and the author's own.

But we must here somewhat abruptly close our examination of this excellent work. Were we to notice every point which well deserves it we should fill a fair-sized volume. Dr. Lunge shows himself *facile princeps* among experts on the manufacture of sulphuric acid and its accessories, at once a thorough practical and a scientific theorist.

CORRESPONDENCE.

THE CHEMISTS' BENEVOLENT FUND.

To the Editor of the Chemical News.

SIR,—Every one of your readers will be glad to know that the challenge sent to the CHEMICAL NEWS early in the year, as to £50 being forthcoming to start a Chemists' Benevolent Fund if nineteen similar or larger subscriptions were offered, has been taken up so satisfactorily that these twenty donations alone amount to £1550. Moreover, other fifties are expected.

Further, promises of sums varying from £2 to £25 amount to £600. These donations, £2150, invested to pay 4 per cent, would yield £86 annually. But promises of annual subscriptions also have been received, varying from 1 to 5 guineas a year, and amounting to £108. Therefore the already promised annual income is £194, representing a capital of £4850.

As a consequence of your kind publication of this letter I shall hope to receive promises of a few more pounds a year or a few more hundreds of capital. So that the net result of the effort to establish this fund within the Jubilee year of the Chemical Society is, say, reckoned as Capital, £5000; reckoned as Annual Income, £200.

Comparing these results with those disclosed by the histories of the benevolent funds of other professional bodies, and bearing in mind the not very large number of the followers of chemistry in Great Britain, it will be obvious that we have made a most satisfactory start in the founding of a Chemists' Benevolent Fund. In short, the project, not altogether a new one, has been received with distinct enthusiasm.

The success so far is due, first, to the generous example set by Mr. Mond, Dr. Gladstone, and others; secondly, to the practical and popular suggestion in March last by the

then President of the Chemical Society, that any such fund should be administered by a representative outside Committee nominated by the Council of the Chemical Society; thirdly, to the support at once accorded by the present Presidents of the four chief Societies of British chemists, namely, the Chemical Society, the Institute of Chemistry, the Society of Chemical Industry, and the Society of Public Analysts. Fifthly, to the fact that in the first circular broadly issued on the subject eighty-six of the 101 officers and members of the Councils of the four Societies just mentioned had already allowed their names to be put forward as supporters of the fund.

Very few refusals of support have been received. No one opposes the scheme. The lines of organisation mentioned in the circular are approved. Two or three theoretical objections have been mentioned, and definitions and details have in a few cases been desired. But only small difficulties incident to the birth and growth of all such funds have been or are likely to be encountered.

Judging by experience it will only be necessary for chemists to apply to wealthy friends interested in chemistry, for consulting chemists to approach industrial clients who have been enriched by chemistry, and for a powerful Committee to appeal to the great brewing, gas-making, water-supplying, and other companies, firms, and corporations whose organisations are closely connected with our science, for the foregoing amount of capital or income to be doubled. The fund might then be left to the growth usual to such funds, if, indeed, any encouragement of further growth should be necessary.

The undersigned would be glad to receive further promises of donations or annual subscriptions within the next ten days, after which the whole matter will be laid before the Council of the Chemical Society.—I am, &c.,

JOHN ATTFIELD.

Watford, Herts; or 17, Bloomsbury Square, W.O.
October 22, 1891.

BEHAVIOUR OF BUTYRIC ACID WITH ALKALINE PERMANGANATE.

To the Editor of the Chemical News.

SIR,—Will you allow me to assure Mr. Johnstone and your readers that in furnishing an analytical journal with an abstract of C. Mangold's paper "On the Estimation of Glycerol" (*Zeit. für Angew. Chemie*, 1891, p. 401), nothing was further from my intention than to give a one-sided report or to suppress facts which might in any way have furnished corroboration of Mr. Johnstone's assertion that butyric acid when boiled with alkaline permanganate yields oxalic acid in more or less quantitative proportions. I have no interest of any kind beyond a strictly scientific one in the matter, and would experience nothing but pleasure if other observers did agree with Mr. Johnstone, although personally I had not been able to arrive at the same results as he did.

From Mr. Johnstone's remarks I cannot but conclude that he is either but imperfectly acquainted with the German language, or that he has not seen Mangold's original paper. I therefore give a literal translation of Mangold's words as far as they touch this matter.

"The presence of butyric acid does not influence the results in any way, as the following experiments show, butyric acid not being oxidised at all by permanganate in alkaline solution in the cold. On continued boiling of butyric acid with excess of alkali and permanganate it yields, as shown by Johnstone (*CHEMICAL NEWS*, vol. lxiii., p. 111), abundant quantities of oxalic acid. But I have satisfied myself by repeated experiments that by following the original method of Benedikt and Zsigmondy the amount of oxalic acid is either not increased at all in the presence of butyric acid or only very slightly, traces at most of butyric acid being attacked under these conditions of temperature and concentration.

"The satisfactory agreement of the whole of the results is seen from the following table:—

	Glycerin p.c.
1. From the specific gravity	96.0
2. Herbig-Mangold method, without heating	96.58
3. " " " " "	96.11
4. Herbig-Mangold " method, with heating ..	95.95
5. " " " " "	95.64
6. " " " " "	95.29
7. In presence of 90 butyric acid to 100 glycerin	95.95
8. " " " " "	96.20."

Clearly, therefore, Mangold does not corroborate Mr. Johnstone. The statement that butyric acid yields oxalic acid is evidently made by Mangold upon Mr. Johnstone's authority, and is not confirmed, but, on the contrary, disproved by Mangold's own observations.

Mangold's analytical figures all agree with each other as nearly as estimations of glycerin by the oxalate method can be expected to agree, and I am sure that the readers of the *CHEMICAL NEWS*, and perhaps Mr. Johnstone, will see that, if "carefully suppressed" by me, they were at all events not suppressed to Mr. Johnstone's disadvantage.—I am, &c.,

OTTO HEHNER.

11, Billiter Square, London.
October 20, 1891.

THE RELATION BETWEEN THE CHEMICAL CONSTITUTION OF CERTAIN ORGANIC COMPOUNDS AND THEIR ACTION UPON THE ULTRA-VIOLET RAYS.

To the Editor of the Chemical News.

SIR,—My attention has been directed to Prof. Dunstan's letter in your issue of July 3rd, 1891, p. 10. I trust that it is not too late to express my regret that he should have considered it necessary to write. Any one who carefully reads my letter of June 5th, p. 309, will observe that I did not suggest that Prof. Dunstan was responsible for the misunderstanding which has arisen with reference to the account of his lecture which appeared in the *Pharm. Journal*, xi, p. 54, 1881. My thanks are due to Prof. Dunstan for having undertaken to send a correction to the *Zeit. für Phys. Chemie*, and also may I add for drawing attention to the fact that the following misleading notice appears in the British Association Report, 1881, "On our Knowledge of Spectrum Analysis":—

CHEMICAL RELATIONS, 1880.—"The Relation between the Chemical Constitution of Certain Organic Compounds and their Action upon the Ultra-Violet Rays" (July 8).—W. R. Dunstan, *Pharm. J. Trans.*, [3] xi., 54—56.

This Report was drawn up with extraordinary care; for example, when it could be ascertained that a paper was read some time before it appeared in print the date of reading as well as its publication in type was noted. It is perfectly evident that the compiler of the list of works in the Report was misled. I must cry *Peccavi* to being one of fifteen on the committee. I believe that the circumstances which gave this lecture the prominence of an original paper were purely accidental.—I am, &c.,

W. N. HARTLEY.

36, Waterloo Road, Dublin.
Oct. 12, 1891.

Contamination of Alkaline Polycarbonates by Heavy Metals, especially Zinc.—Nicolas Huss.—If such carbonates are preserved in metal vessels, the latter are attacked with escape of hydrogen and formation of metallic carbonates. The ammoniacal salts act more strongly than the corresponding potassium and sodium salts. Besides zinc, iron and magnesium are attacked, whilst manganese, chromium, cobalt, nickel, lead, arsenic, &c., are scarcely attacked.—*Zeit. Anal. Chemie*.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 14, October 5, 1891.

On the Simultaneous Existence in Cultures of *Staphylococcus* of a Vaccinating Substance Precipitable by Alcohol, and of a Predisposing Substance Soluble in Alcohol. — A. Rodet and J. Courmont.—The nature of this communication is sufficiently shown by the title.

Zeitschrift für Analytische Chemie.
Vol. xxx., Part 3.

A New Modification of the Dalton-Pettenkofer Method of Determining Carbonic Acid in the Air.—Arsenius Lebedinzeff.—This memoir cannot be reproduced without the seven accompanying figures.

Qualitative and Quantitative Demonstration of Iodides in Urine.—Dr. Adolf P. Jolles.—(a) *Qualitative Detection*.—About 10 c.c. urine are mixed with an equal volume of strong hydrochloric acid, and 2 or 3 drops of a weak solution of chlorine are then added with a pipette in such a manner that they may run down along the inner side of the test-glass. In presence even of very trifling quantities of iodine, there appears at the surface of contact of the two liquids a yellowish-brown ring, which becomes of an intense blue after the addition of a solution of starch. It is known that the presence of indican is shown in the same manner. Still, the presence of indican in whatever quantity cannot mask the above reaction, since the iodine ring has a much more intense colour and appears higher than and separate from the indican ring. The addition of an excess of chlorine is to be avoided. (b) *Quantitative Determination*.—50 c.c. of the urine are evaporated down and the residue carbonised over a Bunsen burner (incineration is not necessary). The carbon is lixiviated with hot water, a solution of silver nitrate is added, and the liquid is acidulated with dilute nitric acid. It is not necessary to add silver nitrate until no further precipitate is formed, since silver chloride is thrown down only when all iodine has been thrown down, and the proportion of chlorine in the urine has no relevance to the method. The precipitate of silver chloride and iodide is filtered off, washed with water containing nitric acid, dried, gently heated in a crucible to fusion, let cool, and weighed. The separation of the silver iodide from the silver chloride is effected after the indirect determination. For this purpose a portion of the mixture is placed in a porcelain boat previously heated and weighed. It is now weighed along with its contents, which are heated to fusion and exposed to a current of chlorine gas in order to convert the silver iodide into chloride. It is let cool in the current of chlorine and the boat is weighed. If there is a loss of weight, D_g , the quantity I of the iodine is found as follows:—For 127 parts of iodine the loss of weight would be 91.5 ($I - Cl = 127 - 35.5 = 91.5$). Consequently we may conclude inversely that if we find a difference of 91.5, 127 parts of iodine were originally present. But since the difference

was not 91.5, but D , it is plain that $I = \frac{127D}{91.5}$.

A New Process for Examining Butters and Fats.—J. König and F. Hart.—This memoir will be inserted at some length.

Belgian Method for Determining the Soluble Phosphoric Acid (i.e., in Water) in Superphosphates.—D. Crispo.—This paper will be inserted in full.

Arrangement for Weighing Oils.—Carl Mangold.—The author gives a figure of a convenient apparatus for this purpose.

On Indicators.—Dr. Otto Foerster.—The author gives the address of a Berlin firm who supply lacmoid of satisfactory quality. He uses as indicator a solution of 3 grms. lacmoid purified by his method, and 5 grms. of Casella and Co.'s naphthol green, in a mixture of 700 c.c. water and 300 c.c. alcohol. Unlike malachite green naphthol green does not precipitate lacmoid, and when mixed in the above proportions it produces a very pure blue in neutral and alkaline liquids, whilst it colours acid liquids an onion peel red.

The Bacteriological Examination of Waters.—Dr. G. Frank.—Already inserted.

The Use of Dry Reactions in Qualitative Analysis.—W. Tate.—(From the *CHEMICAL NEWS*).

The Influence of Inactive Bodies upon the Rotatory Power of Active Substances.—A number of notices by Gernez (*Comptes Rendus*), Haller (*Comptes Rendus*), Farnstoiner (*Berichte Deutsch. Chem. Gesell.*), Brémer (*Recueil de Travaux Chimiques des Pays Bas*), and Bribram (*Monath's Hefte für Chemie*).

Attraction for Precipitates of Places on the Sides of Beakers which have been Rubbed with the Stirring-Rod.—G. Watson.—From the *CHEMICAL NEWS*.

Cause of Band- and Line-Spectra.—H. Kayser (*Annalen der Physik*).—No details are given.

Photography of the Spectra of Metals.—V. Schumann.—(From the *CHEMICAL NEWS*).

The Absorption-Spectra of the Solutions of Iodine in Different Liquids.—H. Rigollot (*Comptes Rendus*).

Colours of the Solutions of Iodine.—H. Gautier and G. Charpy (*Comptes Rendus*).

Connection of the Solubility of Glass with its Composition.—References to several papers in the *Zeit. für Instrum. Kunde, Chemische Industrie, and Thon Industrie Zeitung*.

Aerometer for Complete Submersion.—N. Reggiani (*Atti dei Lincei*).—Already inserted.

Determining the Specific Gravity of Solids.—G. H. Failyer.—(From the *Journal of Analytical Chemistry*).

A New Automatic Mercurial Air-Pump.—Max Stuhl (*Ber. Deutsch. Chem. Gesell.*).—This paper requires the accompanying cut.

Intermittent Mercurial Air-Pump.—K. Prytz (*Ann. der Physik*).—Already inserted.

A New Exploding Furnace.—Couvant and Moscheles (*Chemiker Zeitung*).—The construction of the apparatus cannot be made intelligible without the accompanying cut.

Apparatus for Heating Substances under Pressure.—A. Pfungat (*Chem. Zeit.*), and Hugo Schiff (*ibid.*), where also the illustration is essential. Tubes for exposing substances to high temperatures in currents of gases have been devised by H. N. Warren (*CHEMICAL NEWS*) and A. Richardson (*ibid.*).

Reading Off Burettes.—G. Kottmayer (*Pharm. Post*).—This paper requires the three accompanying cuts.

Capsule-Holder.—P. Boessneck (*Chem. Zeit.*).—An artificial hand for lifting hot evaporating basins, &c.

Self-Acting Apparatus for Shutting off Gas-Flames.—J. Hartkorn (*Chemiker Zeitung*).—Already inserted.

Apparatus for Determining Melting-Points of Fats.—Muter.—(From the *Analyst*).

Constants of Ammonia.—Hans von Strombeck.—(From the *Proceedings of the Chemical Section of the Franklin Institute*).

Detection of Impurities in Mercury.—G. Gore.—(From the CHEMICAL NEWS).

Quantitative Determination of Pyridine Bases in Ammonia.—W. Kinzel (*Pharm. Central Halle*).—Already inserted.

Preparation of Gaseous and Aqueous Hydrobromic Acid.—Notices of papers by A. Recoura (*Comptes Rendus*) Alex. Naumann (*Chemiker Zeitung* and *Ber. Deut. Chem. Gesell.*), Stahlschmidt (*Apotheker Zeitung*), Willgerodt (*Chemiker Zeitung*), and Feit and Kubierschky (*ibid.*).

On α -Naphthol Benzoin as Indicator.—R. Zaloziecki (*Chemiker Zeitung*).—Already inserted.

A New Method for Opening up Silicates.—P. Jannasch (*Ber. Deutsch. Chem. Gesell.*).—This paper requires the accompanying illustration.

Determination of the Final Point in the Titration of Zinc by means of Potassium Ferrocyanide in an Ammoniacal Solution.—Fernando Moldenhauer (*Chemiker Zeitung*).—This memoir will be inserted in full.

NOTES AND QUERIES.

*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Bleaching Powder.—Can any of your correspondents let me know the amount of the total annual production of bleaching powder in Great Britain?—ALFRED MILNEA.

Thermo-Chemistry.—I notice under "Notes and Queries" (vol. lxxiv., p. 155) an enquiry for recent and valuable works on thermo-chemistry. Although I have examined the works in the German language, I believe the last two are translations from the English. As far as I remember I give details:—Horstmann, "Theoretische Chemie u. Thermo-chemie," 1885; price, 13 marks. Naumann, "Lehr- und Hand-buch der Thermo-chemie;" price, 15 marks. Thomsen, "Thermo-chemische Untersuchungen;" price, 51 marks; 4 volumes. These books can be obtained from Meyer and Müller, Berlin, W., Markgrafenstr. No. 51, from whose catalogue I have copied the titles.—S. B.

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G. J. JOHNSON,
President of the Council.

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THE CHEMICAL NEWS.

VOL. LXIV., No. 1666.

A NEW LABORATORY PROCESS FOR PREPARING HYDROBROMIC ACID.

By G. S. NEWTH.

THIS method is a synthetical one, and consists in passing a stream of hydrogen and bromine vapour over a spiral of platinum wire heated to bright redness by means of an electric current. A glass tube, about 7 inches long and 5-8ths of an inch bore, is fitted at each end with a cork carrying a short straight piece of small tube; through each cork is also fixed a stout wire, and these two wires are joined by means of a short spiral of platinum wire, the spiral being about 1 inch long. One end of this apparatus is connected to a small wash-bottle containing bromine, through which a stream of hydrogen can be bubbled. The other end is attached to a tube dipping into a vessel of water for the absorption of the gas, or, if a large quantity of the solution is required, to a series of Woulf's bottles containing water. Hydrogen is first slowly passed through the tube until the air is displaced, when the platinum spiral is heated to bright redness by the passage of a suitable electric current. Complete combination takes place in contact with the hot wire, and the colour imparted to the ingoing gases by the bromine vapour is entirely removed, and the contents of the tube beyond the platinum are perfectly colourless. The vessel containing the bromine may be heated to a temperature of about 50° C. in a water-bath, at which temperature the hydrogen will be mixed with nearly the requisite amount of bromine to combine with the whole of it. So long as even a slight excess of hydrogen is passing, which is readily seen by the escape of bubbles through the water in the absorbing vessels, the issuing hydrobromic acid will remain perfectly colourless, and therefore free from bromine; so that it is not necessary to adopt any of the usual methods for scrubbing the gas through vessels containing phosphorus. When the operation is proceeding very rapidly a lambent flame occasionally appears in the tube just before the platinum wire, but this flame is never propagated back through the narrow tube into the bromine bottle. The precaution may be taken, however, of plugging this narrow tube with a little glass wool, which renders any inconvenience from this cause quite impossible. By this method a large quantity of bromine may be rapidly converted into hydrobromic acid without any loss of bromine, and the operation when once started can be allowed to proceed without any further attention.

COMMENTS ON MR. ROSS'S PAPER ON THE ORIGIN OF PETROLEUM.*

By BOVERTON REDWOOD.

MR. ROSS states that the theories of the origin of petroleum are all founded on some hypothetical process which differs from any with which we are acquainted. In illustration of this statement he asserts that the decomposition of fish could not produce "oil containing paraffin," and he characterises as erroneous the inference that petroleum was formed from the animal matter formerly contained in the fossil shells found in limestone. Presumably he is unaware that many years ago Warren and

Storer, in the United States, obtained by the distillation of a lime-soap prepared from fish-oil a series of hydrocarbons identical with those contained in Pennsylvanian petroleum, and that more recently Engler, and afterwards Engler and Seidner—produced, by the distillation of fish-oil (Menhaden oil, chiefly triolein) and synthetical triolein, under a pressure of several atmospheres, a quantity of artificial petroleum. In his earlier experiments Engler isolated pentane, hexane, and heptane from the distillate, and in the later experiments conducted in association with Seidner, on a fairly large scale, several higher members of the paraffin series were separated, as well as olefines. During the distillation a considerable quantity of permanent gas, largely composed of methane, was evolved. The artificial petroleum, which was described as a nearly colourless fluorescent liquid, apparently resembling ordinary American kerosene in physical characters, was not only examined chemically, but was obtained in sufficient quantity to admit of its being practically tested by burning in lamps in comparison with the Pennsylvanian petroleum oil of commerce, and its illuminating power in two well-known German lamps was found to be high in relation to the consumption of oil.

It is worthy of note that Mr. Peckham, after a careful examination of the various "chemical" theories expressed in relation to them much the same opinion as that held by Mr. Ross in relation to all other theories than his own, viz., that they required the assumption of operations nowhere witnessed in Nature or known to Technology. In this connexion it would be interesting to know what direct experimental proof Mr. Ross has obtained of the correctness of his views. Mr. Peckham further pointed out, as objections to an inorganic theory, that it would not be expected that a process yielding a diversity of products, under slightly varying circumstances, would furnish a uniform result over a very wide area, or that the same process acting upon similar materials would produce the very different varieties of petroleum met with. Thus samples of Pennsylvanian petroleum of the same density obtained from widely separated localities furnish identical results upon analysis, and the same may be said of Californian petroleum; yet the two descriptions of petroleum are very dissimilar.

As Mr. Topley, F.R.S., took occasion to point out in a recent paper on the Sources of Petroleum and Natural Gas, the American geologists and chemists are agreed that petroleum has resulted from the decomposition of the fossils in the shales and limestones of the Silurian, Devonian, and Lower Carboniferous rocks, chiefly the remains of animals, but in some cases also the remains of plants; that the gas and petroleum thus formed are stored in porous sandstones and limestones, and are prevented from escaping by a covering of impervious shale.

The organic theory may certainly be said to be that which receives the largest measure of support not only in America, and in relation to American petroleum, but in all countries and in relation to all petroleum. It may, however, be safely asserted that the process by which petroleum has been formed has not been the same in all cases. It is quite possible that petroleum may in some cases be of inorganic origin, and the distinguished authorship and support of certain of the inorganic theories is an important feature of the case.

In some instances the petroleum is apparently indigenous to the rocks in which it is found, while in others it appears to be a distillate from strata lying far below the formation in which it is stored.

The not unusual association of mud-volcanoes with petroleum deposits surely cannot be accepted as a proof of the volcanic origin of petroleum, and the outflow of petroleum accompanied by natural gas which occurs in such localities may be due to the action of the volcanic heat upon hydrocarbons formed long ago.

Mr. Ross expresses a doubt whether room could have been found in beds of porous sandstone for the immense

* A reproduction of the remarks made by Mr. Redwood when the Paper in question was read before the British Association, Cardiff Meeting, 1891, Section G.

quantities of petroleum raised in America, and he suggests that the oil may have been stored in vast receptacles carved by volcanic water out of former beds of rock salt adjoining the limestone. Dr. T. S. Hunt estimated the amount of oil held in the Niagara limestone of Chicago, and found it to be 4.25 per cent. On this basis the quantity of oil in each square mile of the oil-bearing rock would be 7,750,000 barrels. Again, Mr. J. F. Carll has shown that the pebble sand will absorb 1.15th to 1.20th of its bulk of oil, and this, at a very moderate estimate of the average thickness of the oil-sands in the neighbourhood of Oil Creek, would give a storage capacity of 9,600,000 barrels per square mile, which, as Mr. Peckham has pointed out, is quite adequate to the requirements of the most exceptional cases known. No doubt in some instances the sudden dropping of the tools in the process of drilling indicates the existence of cavities or fissures, but there can be very little doubt that the oil is usually stored in porous rocks.

Mr. Ross states that practical men in this country distrust the permanence of the supply, and hesitate to adopt petroleum for many useful purposes, the object of his paper being to dissipate that distrust by suggesting an explanation of the mystery surrounding the origin of the material. The object is doubtless a laudable one, though in view of the immense undeveloped sources of petroleum, in the existence of which there is good reason to believe, it may be questioned whether the distrust, if it exists, has any good foundation. Obviously it would be satisfactory to feel that the process of formation of petroleum from inorganic substances is now in operation; but the theory which Mr. Ross has propounded is scarcely likely to carry conviction to the minds of any who experience the distrust to which he alludes.

THE REDUCTION OF OXYGEN COMPOUNDS BY MAGNESIUM. FORMATION OF METALLIC HYDRIDES. By CLEMENS WINKLER.

THE author recently drew attention to the remarkable behaviour of cerium, which in the nascent state combines very eagerly with hydrogen. Not less striking is the fact that other quadrivalent elements, such as zirconium and thorium, behave similarly, and that also lanthanum, which belongs to the third group, combines with hydrogen as readily as cerium and with exactly the same phenomena.

In accordance with the trivalence of lanthanum, and taking its atomic weight $\text{La} = 138$, the author ascribed to lanthanum hydride the formula La_2H_3 , but after vain attempts to combine other members of the third group, such as aluminium and yttrium, and some of the second group, *e.g.*, Ca and Ba, with hydrogen in the same manner, he felt inclined to infer from its surprising similarity of behaviour with cerium that lanthanum might possibly belong to the quadrivalent elements, in which case the formula of lanthanum hydride would be LaH_2 .

Meantime, Brauner maintained the trivalence of lanthanum, and the atomic weight $\text{La} = 138$, and his expositions, joined to the author's own researches, induced the latter again to regard lanthanum as trivalent and its hydride as La_2H_3 . It appeared that the property of combining in the nascent state with hydrogen belongs not only to lanthanum but to other members of the third group, certainly to yttrium and probably to scandium and ytterbium.

At Brauner's inducement I returned to the members of the second group and again endeavoured to produce their hydrides. Brauner has informed me in a letter under date April 30th last, that he considered the existence of a barium hydride and perhaps of a caesium hydride as not improbable, pointing out that the discovery of these compounds would form a brilliant confirmation of the periodic law, as there would result the following series—

	I.	II.	III.	IV.
Metal	Cs	Ba	La	Ce
Oxide	Cs_2O	Ba_2O_2	La_2O_3	Ce_2O_4
Hydride	Cs_2H	Ba_2H_2	La_2H_3	Ce_2H_4

or—



as these hydrogen compounds unquestionably represent polymers of the simple formulæ.

Group I.

As for caesium and the other members of the first group which here come in question I found it at first impracticable to combine them with hydrogen in the nascent state, *i.e.*, by reduction of their oxides in an atmosphere of hydrogen by means of magnesium. The reduction of the lithium and sodium hydroxides and carbonates takes place with dangerous violence, and that of the corresponding compounds of potassium and rubidium with so considerable a liberation of heat that the hydrides of these metals cannot resist its decomposing action.

Cesium.—The formation of caesium oxide, Cs_2O , would be possible only by means of metallic caesium. As this substance was not at my disposal I confined myself to ascertaining the behaviour of magnesium with caesium hydroxide and carbonate in an atmosphere of hydrogen.

On heating together a mixture of 150 parts (1 mol.) caesium hydroxide and 24 parts (1 atom) of magnesium in a current of hydrogen fire appeared, and there was formed behind the boat a metallic mirror consisting chiefly of potassium. The residual sintered mass seemed composed of a mixture of caesium and magnesium oxides. On operating upon caesium carbonate the result was similar.

Group II.

It appeared especially important to ascertain the behaviour of nascent metals of the second group with hydrogen, since we had hitherto not the slightest evidence concerning their power of forming hydrogen compounds. Though former experiments had not shown a behaviour similar to that of cerium and lanthanum, I have now the satisfaction of communicating that I have succeeded in combining all the bivalent elements which come here under consideration with hydrogen, at least to a certain degree. This combination ensues in general so slowly that it may at first escape recognition. The heavy metals of the second group, zinc, cadmium and mercury, the oxides of which are reduced by magnesium with explosive violence, could not come into account, the investigation being limited to the metals of the alkaline earths.

The process adopted was in all cases the same. If one of the oxides, *e.g.*, calcium oxide, is heated to redness in an atmosphere of hydrogen, along with the quantity of magnesium powder required for its reduction as it was done with cerium, not the slightest absorption of gas is perceived at first, so that the pinch-cock at the end of the combustion tube must be frequently eased to prevent the liquid in the washing and drying flasks from being forced back. But after the heat has been applied for some time this movement ceases and a few bubbles escape through the washing-flasks. The process varies greatly in rapidity and in some cases has to be continued for hours.

Glucinum and magnesium combined with hydrogen only to the respective extents of 14.96 and of 6.42 per cent. Of calcium 61.52 per cent of the substance operated upon was converted into hydride, and of strontium 94.91 per cent. Barium oxide was converted into hydride to the extent of 94.66 per cent.

From the above facts it appears that all the bivalent elements, in as far as they belong to the class of so-called light metals, are capable of forming hydrogen compounds. The formation is in most cases slow, unattended with striking phenomena, and is effected at moderately high temperatures not exceeding bright redness. Indications are present that a further increase of temperature promotes the formation of hydrides, and besides the disposi-

tion of the elements in question to form hydrides increases directly as their atomic weights.

It seems striking that all the hydrides above mentioned appear as dull, earthy masses, whilst the hydrogen compounds of the alkali metals described by Troost and Hautefeuille, Na_4H_2 and K_4H_2 , are silvery white and of a metallic lustre.

It must for the present remain undecided whether the hydrogen compounds of the bivalent elements should have the general formula $\text{R}''\text{H}$, or $\text{R}''_2\text{H}_2$, or $\text{R}''_4\text{H}_4$, or if they require a still further multiplication. In any case the proof that such compounds exist is of general chemical interest as well as important as regards the periodic law and the doctrine of valences. But it has a still further significance, since it leads our thoughts and contemplations to the process of creation, to the cosmic structures of different stages of age and development, existing at infinitely higher temperatures than our earth, far advanced as it is in the process of refrigeration. The spectroscope tells us of the very prominent part which hydrogen has played and still plays in the construction of worlds. It reveals to us in the probably hottest stars the presence of just those elements about which we now know that they are able to form hydrogen compounds at very high temperatures,—compounds which are stable in fire.

The same compounds meet us in the sun's atmosphere, which is so much more accessible to spectroscopic examination. If we see in the protuberances escapes of gas, which contain hydrogen, magnesium, and calcium (the last in predominating quantity), the assumption no longer seems unjustifiable that they consist of calcium and magnesium hydrides, even if in a state of dissociation. When projected up to relatively cold elevations they suddenly undergo catagenesis, whereby the marvellously rapid disappearance of these gaseous masses and possibly other phenomena of the sun's surface may be explained. In any case it is an advantage that we can now deal with definite hydrogen compounds of those metallic elements, such as calcium and magnesium, which predominate in the atmosphere of the sun and the other fixed stars.

As Janssen's spectroscopic observations undertaken on the summit of Mont Blanc have shown, oxygen seems absent in the sun or in its gaseous envelope. But even if present it would not exclude the possibility of the simultaneous presence of the above mentioned hydrides of the earthy metals, since these may be permanent and stable at temperatures above the dissociation heat of water. But if we conceive of a heavenly body in a state of heating in which, e.g., calcium hydride can exist along with free oxygen—a heat at which our earth once existed—and if we suppose this orb undergoing refrigeration, a point will be reached at which the calcium hydride ignites with an outburst of flame, exhibiting the spectacle of a burning world, like that seen in 1866 in a star of *Corona borealis*.

And if we consider a more advanced refrigeration such as our earth has already undergone in ages long since past, the combustion product of hydrogen, the water, will begin to react chemically upon the combustion product of the calcium, lime and calcium hydroxide will be formed, or the origin of other calcium salts will be effected with the co-operation of other elements such as carbon or silicon, and the water will remain in excess in a free state, as it has been the case on our earth. Such processes as the last mentioned lie so near our comprehension that we can interpret them, since we can produce them artificially. By the discovery of the heat-resisting hydrides of the earthy metals we may, perhaps, in the future approach nearer to an understanding of the processes in the glowing atmospheres of the fixed stars; and even if this still leaves much scope to the imagination, we must remember that the imagination begins to be permissible in science as long as it is based upon actual observation.—*Berichte der Deutsch. Chem. Gesell.*, vol. xxiv., p. 1966.

A CONTRIBUTION TO THE QUANTITATIVE DETERMINATION OF SULPHUR.

By F. P. TREADWELL.

In sulphides which are soluble in dilute acids the sulphur is now generally determined either by the oxidation of the liberated hydrogen sulphide, by means of an alkaline solution of hydrogen peroxide, precipitating the sulphuric acid formed as barium sulphate, or the hydrogen sulphide is determined volumetrically, according to Dufusquier and Bunsen iodometrically, or by the alkalimetric process of Eliasberg. These elegant methods, however, are restricted to soluble sulphur compounds. In insoluble sulphides sulphur could not hitherto be determined by the above processes.

The author has found a very simple method, according to which sulphur can be readily expelled from all insoluble sulphides in the state of sulphuretted hydrogen, and determined by one of the above processes. The sulphide, mixed with an excess of iron, is heated for five to ten minutes to dull redness in a current of dry carbonic acid, and the ferrous sulphide formed is decomposed, when cold, by means of hydrochloric acid. A tube of very infusible glass serves for the introduction of the carbonic acid. The iron used is the ordinary commercial "ferrum reducum," which before use is ignited in a current of dry hydrogen. Prior to the determination of the sulphur a blank experiment is made with the materials which are to be used, in order to ascertain their proportion of sulphur. This is done as follows:—

Into a porcelain crucible (made at the Bayeux Works at the price of 30 frs. per hundred) are put 3 grms. of iron powder. The crucible, according to Loewe's proposal, is supported upon a piece of sheet asbestos, in the middle of which there is cut a hole exactly fitting the crucible, which is heated for ten minutes at incipient dark redness in a current of carbonic acid. After being allowed to cool, still in a current of carbonic acid, the crucible with its contents is placed in an Erlenmeyer flask holding about 400 c.c., and provided with a caoutchouc stopper with a double perforation. Through the small aperture passes the gas delivery tube having a small condensation bulb, above which it is bent downwards at an angle of 15° , so that its lower end reaches lower than the bottom of the flask. Through the other perforation passes a tube reaching down to the bottom of the flask and ending above in a globe funnel with a glass cock. The lower end of the gas delivery tube is connected with a Kipp hydrogen apparatus, and a powerful current of hydrogen is passed through for five minutes, whilst the cock of the globe funnel is left open. The cock funnel is then closed, the flexible tube is removed from the gas delivery tube, and the latter is connected with two Fresenius-Vollhard absorption apparatus. The first of these vessels is filled with 50 c.c. of the purest 2 per cent hydrogen peroxide and 10 c.c. of binormal ammonia, whilst the second vessel contains 10 c.c. of ammonia of the same strength. Into the globe funnel are poured 100 c.c. of dilute hydrochloric acid previously boiled (1 : 5), which is slowly let down into the flask. A liberation of gas begins at once and is assisted by a gentle heat, so that three or four bubbles per second pass through the absorbent vessels. In $1\frac{1}{2}$ to 2 hours the development of gas is completed, when a current of pure hydrogen is allowed to pass for half an hour through the globe funnel tube. The contents of the absorbent apparatus are poured into a beaker, covered with a watch-glass, and boiled for fifteen minutes, acidulated with hydrochloric acid, and evaporated to dryness in a porcelain capsule on the water-bath. A few drops of concentrated hydrochloric acid are added to the dry mass, which is dissolved in hot water, filtered, and precipitated with barium chloride.

In the author's experiments the amount of barium sulphate thus found was merely 5 m.grms., which was deducted in the subsequent determinations. In executing

the actual analysis a little iron-powder is first placed in the decomposition crucible, then the substance, then again iron-powder, and the whole is mixed with a platinum spatula. The mixture is covered over with iron-powder, and the operation is completed as in the blank experiment.

The method is applicable to arsenio-sulphates. It cannot be used in the technical analysis of pyrites, as the sulphur present in every combination—*e. g.*, barium sulphate—is determined. In case of arseniferous minerals, &c., hydrogen arsenide is evolved in abundance, whence in such case the escaping gas, after removal of the absorption vessels, is passed into an ammoniacal solution of silver.—*Berichte Deutsch. Chem. Gesellschaft*, vol. xxiv., p. 1937.

DECOMPOSITION OF CHROME ORE BY MEANS OF THE ELECTRIC CURRENT.

By E. F. SMITH.

Two years ago the author mentioned that an intimate mixture of chrome iron ore and melted potassa is decomposed by the introduction of the electric current, and that the chromium oxide present is converted into soluble potassium chromate. The earliest attempts were made with a current of 1 ampère. The oxidation of the mineral was apparently completed in 15 minutes, but the wish to economise time by increasing the current led the author astray, and many decompositions, fruitless as well as successful, were made before the most satisfactory conditions were ascertained. It was found that a more powerful current acted chiefly upon the oxides of iron contained in the ore and the potassa employed, liberating larger or smaller portions of the respective metals. The occurrence just mentioned seems to take place after a partial decomposition of the mineral, so that a little of the chrome ore always remains undecomposed.

The following method was found after many experiments to give good results:—

Method of Oxidation.—30 to 40 grms. caustic potassa are brought to fusion in a nickel crucible 1½ inches in height and 2 inches in width, and gently heated until the excess of water is evaporated. The crucible is then set upon a heavy ring of copper wire in connection with the anode of a battery.

During the decomposition the crucible is gently and uninterruptedly heated by means of a small flame. The mineral is weighed out upon a watch-glass and is then carefully placed upon the liquid potassa by means of a camel's hair pencil. The crucible is covered with a perforated watch-glass, and the platinum rod connected with the cathode of the battery is let down into the melted mass, thus producing the current. Portions of the melted mass are projected against the under side of the watch-glass, but the liquid soon collects in drops and falls back into the crucible, and thus restores any traces of ore which have been projected upwards by the bursting of the gas bubbles.

Experience shows that it is preferable to use the crucible itself as an anode. Before the current is finally interrupted it must be reversed by means of a commutator, which is left permanently in the current along with a Kohlrausch ampère-meter. This is necessary because metal is deposited upon the cathode and contains particles of ore which are thus withdrawn from the oxidising process. By reversing the current these particles of ore are set at liberty and made capable of oxidation.

The quantity of ore to be taken for analysis varies from 0.1—0.5 gm. The ore used for oxidation must be ground quite fine. In the author's experiments the ore was never used in such a fine state of comminution as is prescribed in order to obtain a complete decomposition by other methods.

For the quantity above indicated the current must not exceed 1 ampère. As for the time needed for oxidation the quarter of the ore is indubitably decomposed in 15 minutes, but to effect a complete decomposition of the ore a time of 30—40 minutes is recommended. Much depends on the resisting power of the sample. In this respect chrome ores vary exceedingly,—a difficulty which has to be overcome in every method for their analysis. Half an hour at least should be allowed for completing an oxidation by this method.

As the decomposition proceeds the melted potassa takes a deeper yellow; the part which climbs up on the edge of the crucible and the watch-glass resembles a cauliflower.

The current may now be interrupted. When this has taken place the platinum rod (the cathode) is lifted out the liquid, the watch-glass is carefully lifted off the crucible with nickel forceps, its lower surface is rinsed with water, and the washings are collected in a beaker. The crucible is then removed from the copper ring and set upon a marble plate to cool. The platinum cathode must also be washed with water. It appears black in consequence of the deposit of metallic iron which has been formed upon it.

It is judicious to dissolve this coating in dilute hydrochloric acid in order to be satisfied that no undecomposed ore is present in it.

When the crucible is cold it is placed in a beaker holding about 300 c.c., covered with water, and set to digest upon a warm plate. In a few minutes the contents of the crucible are entirely dissolved and the crucible itself may then be removed from the liquid. It contains, beside an excess of potassa, potassium aluminates, silicates, manganates, and chromates. The insoluble matter in suspension consists chiefly of iron oxide.

After the alkaline solution has been heated for a time on the plate, the insoluble part is filtered off and thoroughly washed in boiling water. The vessel containing the soluble salts is set aside, and the portion insoluble in water is treated with hot hydrochloric acid. It must dissolve completely without leaving a residue. If this is not the case the decomposition is incomplete.

Determination of the Chrome.—The chrome in the yellow alkaline filtrate may be determined either gravimetrically or volumetrically. In his more recent determinations the author used exclusively the latter method. For this purpose the chromic solution was acidified with sulphuric acid, and a weighed quantity of ammonium ferrous oxalate was added. An excess of the latter was determined by normal potassium bichromate. Potassium ferrocyanide was used as reagent. In some cases the excess of ferrous salts was determined with a solution of potassium permanganate, but this method was abandoned, as the final reaction could not be recognised with sufficient exactness.—*Berichte der Deutschen Chem. Gesellschaft*, vol. xxiv., p. 2182.

PROPERTIES OF PRECIPITATES, &c.*

By E. WALLER, Ph.D.

(Continued from p. 210).



Rem.—Precipitant, $PtCl_4$.

More strongly coloured than the corresponding ammonium salt, but otherwise resembling it in general characters. Like that compound, it is sometimes dissolved in hot water, and the solution evaporated in a weighed capsule so as to dispense with weighed filters.

Cond.—Solution should be cold, alcoholic, and should contain preferably only sodium salts other than KCl.

* From *School of Mines Quarterly*, xii., No. 3.

Chlorides or HCl should be present. Small amounts of Mg or Ca are permissible, though disadvantageous.

Sol.—Somewhat soluble in cold, more so in hot water. Insoluble in strong alcohol and in ammonium salts. Solubility increased by acid or alkali, diminished by PtCl_4 or Na_2PtCl_6 .

Contam.—NaCl and other salts (as sulphates) not soluble in alcohol. Such contaminants are most readily removed by washing with aqueous solution of NH_4Cl , previously saturated with K_2PtCl_6 .

Ign.—Alone, it is imperfectly converted to KCl and spongy platinum; with a reducing agent (as $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), the conversion is complete. The heat should not be too rapidly raised. If ignited in platinum, too high a heat may fuse the finely-divided metal to the platinum vessel. After ignition, the KCl formed must be washed off with water before weighing.

NaCl.

Rem.—See *Rem.* under KCl.

Cond.—As for KCl.

Sol.—Soluble in water; much less so in strong HCl or alcohol. Less soluble in these menstrua than KCl.

Contam.—KCl (see KCl) or other non-volatile salts.

Ign.—Decrepitates violently on heating unless very thoroughly dried. Fusible at full red heat, and volatilised at a temperature but little above its point of fusion. The temperatures of fusion and volatilisation are, however, perceptibly higher than with KCl. Becomes slightly alkaline on fusion from loss of Cl.

Na_2SO_4 .

Rem.—The suggestions as to K_2SO_4 throughout are applicable also to Na_2SO_4 (see K_2SO_4), even to the formation of NaHSO_4 by evaporation with excess of H_2SO_4 and ignition.

CaC_2O_4 .

Rem.—Usual precipitant $(\text{NH}_4)_2\text{C}_2\text{O}_4$. The solution of the reagent had best be boiling hot when added. Precipitated cold or in very dilute solutions, it separates in a very fine powder. In any case, boiling for a short time and then adding a few drops of ammonia is advisable before proceeding to filter. If precipitated in boiling alkaline solution, the solution bumps vigorously. Enough oxalate should be added to convert all Mg present into $\text{Mg}_2\text{C}_2\text{O}_4$.

Cond.—Best precipitated in a boiling neutral solution, which should contain only Mg and alkalis besides the Ca.

Sol.—Dissolved by mineral acids, slightly soluble in acetic. Somewhat soluble in MgCl_2 . Insoluble in MgC_2O_4 . From its solutions in mineral acids, ammonia or other alkalis precipitate it unchanged.

Contam.— MgC_2O_4 , which is removed by re-solution in HCl and re-precipitation by ammonia. If the proportion of Mg present is large, this re-solution and re-precipitation may have to be repeated two or three times. Precipitation in a solution barely acid with HCl is most effective in separating from Mg.

Ign.—Affords first CaCO_3 , afterward CaO. Under ordinary circumstances the product is a mixture of the two. To obtain CaO it is necessary to ignite for some time over a blast lamp. To obtain CaCO_3 , it is ignited moderately, and repeatedly moistened with ammonium carbonate, and gently ignited after each addition.

Ignited with H_2SO_4 it affords CaSO_4 , which is frequently partially reduced to CaS by ignition with C, requiring further treatment with H_2SO_4 and ignition. The easiest mode of management is to transfer the filter paper containing the precipitate still wet to an ordinary fusion crucible, and wet down with concentrated nitric and sulphuric acids. Then expel the excess of acid with a gentle heat, and finally ignite. A second treatment with H_2SO_4 is often necessary. Instead of H_2SO_4 , a strong solution of $(\text{NH}_4)_2\text{SO}_4$ containing free ammonia and about 2 grms.

NH_4Cl per 100 c.c. has been recommended (*vide Crookes's "Select Methods," Second Edition, p. 47*).

CaCO_3 .

Rem.—Usual precipitant $(\text{NH}_4)_2\text{CO}_3$. For separation or determination of CO_2 , the reagent is CaCl_2 with ammonia. Usually obtained for separation. At first it separates in flocculent or amorphous form, but after a short time assumes a crystalline form. This change is hastened by warming gently.

Cond.—Large proportions of alkaline salts, especially citrates, and of magnesium salts, should be avoided. An alkaline solution is of course necessary.

Sol.—Soluble in water containing CO_2 ; very soluble in all acids; decomposed and dissolved by NH_4Cl , slowly in the cold, quickly if hot. Insoluble in water containing ammonium carbonate with ammonia.

Ign.—Converted to CaO as described under $\text{Ca}_2\text{C}_2\text{O}_4$. The change is more readily effected if some carbon is mixed with it.

MgNH_4PO_4 .

Rem.—Usual precipitant for Mg, Na_2HPO_4 ; for P_2O_5 (ortho), "magnesia mixture," preferably that made with MgCl_2 .

Should be crystalline; if flocculent, some contaminant is present. When the proportion of precipitate which can form is small relatively to the bulk of the solution, some hours are necessary for complete separation.

Completeness of precipitation much accelerated by cold and agitation.

When washed as usual with diluted ammonia, alkaline phosphate (Na_2HPO_4 , &c.) is not very rapidly removed, the salt being less soluble in ammonia than in water.

Cond.—Absence of silica or any bases other than alkalis. NH_4Cl or ammonium salts should be present.

Sol.—Solution should be cold for precipitation and filtration. Soluble in acids, even when weak, in hot solutions, and to some extent in cold water; insoluble in dilute ammonia.

Contam.—Silica and $\text{Mg}(\text{OH})_2$ or basic salts of Mg. The latter is only likely to occur when the precipitate is used for the purpose of determining P_2O_5 or P. The difficulty is avoided by adding the Mg mixture (preferably the chloride) slowly with stirring. Silica may be weighed and deducted after ignition, weighing and dissolving in acid. MoO_3 may also occur when the molybdate separation has preceded.

Ign.—Should be well dried before igniting. If heated too rapidly some loss may result from too rapid decomposition. If the filter paper is allowed to burn with flame, some particles of the precipitate (in weighable amount) may be mechanically carried off. The precipitate has afterward a tendency to sinter together at a moderately high heat, thereby preventing the oxygen of the air from penetrating the mass and oxidising the carbon, the precipitate being left grey or black. The best mode of managing is to expose the precipitate for some time to a dull red after the carbonisation of the paper, and finally finish with the full heat of the Bunsen burner. If the precipitate comes black repeated moistening with nitric acid and cautious ignition is to be recommended.

$\text{Mg}(\text{OH})_2$.

Rem.—Usual precipitant $\text{Ba}(\text{OH})_2$ for separation from alkalis when these are to be determined. The $\text{Ba}(\text{OH})_2$ should be tested for NaOH, which is not infrequently present.

Cond.—Alkaline solution moderately concentrated, containing no NH_4 salts.

Sol.—Dissolved by acids or ammonia salts. Precipitation partly prevented by presence of organic salts, citrates, tartrates, sugar, &c.

Contam.—Usually unimportant, the object generally being to remove from the solution MgO and all substances except those readily separable by ammonium carbonate.

BaSO₄.

Rem.—Precipitant for SO₃, BaCl₂; for Ba, H₂SO₄.
Precipitated in an extremely fine state of division (runs through filter paper) if formed in cold or dilute solutions, or such as contain ammonia salts. Forms slowly if small in amount.

The tendency of the precipitate to creep up the side of a beaker may be checked by adding a drop of HCl.

Cond.—Hot solution acidified with HCl. Hydro-fluo-silicic acid or silica should be absent, also large proportions of calcium salts, or salts of the (NH₄)₂S group of bases.

Sol.—Soluble in concentrated H₂SO₄, in HCl when moderately strong and hot, and in HNO₃ even when tolerably dilute. It is also soluble in hot Fe₂Cl₆, in alkaline and alkaline earth nitrates, citrates, and salts of some other organic acids.

Insoluble in water, in very dilute HCl, and in acetic acid.

Contam.—The especial difficulty with BaSO₄ is its tendency to carry with it other substances, as alkaline and alkaline earth nitrates, chlorates, sulphates, and chlorides. Potassium salts give more trouble in this respect than sodium salts. The precipitate may also contain silica, and basic ferric, aluminic, or chromic compounds.

Repeated boiling up with very dilute HCl assists in removing some of these to a considerable extent, though there is some danger of dissolving some of the precipitate by this treatment. Washing alternately with hot dilute HCl and with cold water is often advantageous. Stolba's method of purifying the precipitate consists in digesting (after washing) for ten to fifteen minutes at a boiling heat, with 40—50 c.c. of cold saturated solution of Cu(C₂H₃O₂)₂ and acetic acid, filtering, and washing free from Cu (*vide* Crookes's "Select Methods," second edition, p. 492). Sloane recommends for purification from iron, to decant the supernatant liquid closely, then add 5 or 10 c.c. of concentrated HCl, and boil for one minute, dilute, and after nearly neutralising with ammonia, filter and wash thoroughly (*Four. Amer. Chem. Soc.*, iii., 37). Archbutt advises to precipitate warm (not boiling), allow to stand until thoroughly cold and the precipitate has settled well, then to filter and wash with cold water (*Four. Soc. Chem. Ind.*, ix., 25). Jannasch and Richards assert that no correct determination of SO₃ can be made in the presence of Fe, because the precipitate always contains more or less of a double barium iron sulphate, from which SO₃ is expelled on ignition. To avoid errors they therefore recommend the previous removal of the iron by ammonia (*Four. Prac. Chem.*, [2], xxxix., 321), (*vide* also Lunge, *Zeit. Angew. Chem.*, 1880, 473). Zeigler (*Pharm. Central.*, 1881, p. 555) recommends the addition of some AgNO₃ to the solution (containing chloride), that the AgCl may enclose and carry with it the particles of BaSO₄. After washing with water the AgCl may be dissolved off with ammonia.

Ign.—With C some BaS invariably forms. The difficulty may be remedied by adding a few drops of fuming HNO₃ to re-oxidise the S, and igniting again, or better by re-igniting after the addition of a drop or two of concentrated H₂SO₄.

BaCO₃.

Rem.—At first amorphous, it assumes almost immediately the crystalline form, in which condition it does not affect alkalimetric indicators.

Cond.—Alkaline solution.

Sol.—Soluble in water containing CO₂ and in acids. Also taken into solution by NH₄Cl and some other ammonium salts, especially on boiling. Insoluble in a mixture of ammonium hydrate and carbonate.

Contam.—MgCO₃ if much is present, and carbonates of fixed alkalis if present.

Ign.—Converted imperfectly to BaO, unless mixed with carbon, when the change occurs readily.

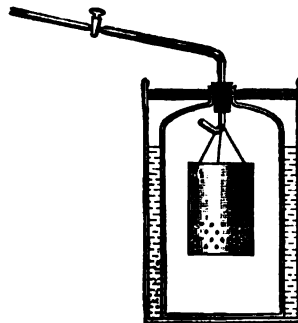
(To be continued.)

SIMPLEX GAS GENERATOR.

By C. G. MOOR.

THIS new pattern gas generator possesses several advantages over those now in use. It may be used equally well to prepare hydrogen, carbonic acid gas, chlorine (using the compressed chloride of lime), or sulphuretted hydrogen.

The last-mentioned can best be prepared by using commercial hydrochloric acid mixed with an equal bulk of water. The apparatus is easy to clean and charge, delivers a drier gas than most other forms of generator, and the liquid cannot travel up the gas tube. The parts may be had separate.



To charge, take out bell-jar and unhook perforated pot, fill it with the solid and replace, pour acid into outer jar till about half full.

The solid may be any size or shape provided it is not dust. Any part of the apparatus can be had separately to replace breakages.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1891.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, October 8th, 1891.

SIR,—We submit herewith the results of our analyses of the 181 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from September 1st to September 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 181 samples examined, the whole were found to be clear, bright, and efficiently filtered, excepting one, which was recorded as "very slightly turbid."

The satisfactory condition of the water supply to the Metropolis, recorded now for several consecutive months,

continued to be maintained during the month of September; although, indeed, the individual results obtained exhibited a somewhat greater degree of variation than has been noticeable for some time previously. Thus in the case of the Thames-derived supply, the mean proportion of organic carbon was found to be 0.129 part in 100,000 parts of the water, with a maximum of 0.150 part in any single sample examined; while the mean amount of oxygen absorbed was found to be 0.076 grain per gallon of water, with a maximum of 0.145 grain in any single sample examined. The highest results were afforded by the examinations made during the middle of the month; and the figures resulting from the separate modes of examination were less closely parallel than usual, those expressing the amounts of oxygen absorbed agreeing best with the determinations of the colour-tint of the water.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

ON THE OCCURRENCE OF NITROGEN IN URANINITE, AND ON THE COMPOSITION OF URANINITE IN GENERAL.*

By W. F. HILLEBRAND.

General Introductory Remarks.

WHEN the work which is described in the following pages was commenced in 1888 it was simply as an analysis of a fragment of a large crystal of uraninite from Glastonbury, Connecticut, without thought of further extension. Thoria had been found in it, and quantitative analysis was made in order to learn if possible whether this belonged to the uraninite or was due to an accidental admixture of thorium silicate as found by Penfield (*Am. Jour. Sci.*, [3], 1882, xxiv., 250) to be the case, at least in part, for the thoria in monazite from Portland, Connecticut, and Amelia County, Virginia. It was hereby established that the 10 per cent of thoria found was a constituent of the uraninite, and the unexpected discovery was made that no formula in the slightest degree corresponding to that found by Comstock (*Am. Jour. Sci.*, [3], 1880, xix., 220) for the Branchville, Connecticut, uraninite, and by Blomstrand (*Geol. För. Förh.*, 1884, vii., 59, and *Jour. Prakt. Chem.*, 1884, xxix., 191) for the Norwegian and Bohemian varieties, could be assigned to this from Glastonbury. The hitherto unanalysed uraninite formerly found at Black Hawk, Colorado, was then examined, and was likewise not referable to the orthouranate formula of Blomstrand. No thoria was found in it, but instead about 7 per cent of zirconia. In both cases about 60 per cent of UO_2 had been found, whereas the highest percentage given by any other analyst was in the neighbourhood of 54 per cent for the Branchville variety. My own experiments had shown such extraordinary variations in the percentages of UO_2 found by the ordinary method of decomposing with sulphuric acid in sealed tubes filled with carbonic acid, and titrating with potassium permanganate, that a re-examination of the Branchville mineral seemed desirable.

Profs. Brush and Dana, of New Haven, very kindly placed at my disposal the remainder of their material from that locality, it being the same lot from which Comstock had selected his sample for analysis. While different samples showed different amounts of UO_2 , the results were from 10 to 18 per cent higher than Comstock's, and, moreover, about 7 per cent of thoria was found which had been entirely overlooked by him. This latter, as in the Glastonbury mineral, was not referable to any thorium

silicate, nor to a phosphate, but belonged to the uraninite. Comstock's formula, $3RO_2 + 2RO_3$, for the Branchville uraninite was of course hereby invalidated. Of North American occurrences of this mineral it only remained to examine that from North Carolina. From the Black Hills, Dakota, where it has been reported to occur, I have been unable to procure specimens, and the same can be said of the—at that time unknown—Llano County, Texas, locality, whence a closely allied mineral, nivenite, has recently been described by Hidden and Mackintosh (*Am. Jour. Sci.*, 1889, [3], xxxviii., 482). Owing to its evident alteration it was not expected that light would be thrown on the question of original composition by an examination of the North Carolina material, but the presence or absence of thoria could be ascertained, as it was affirmatively by finding that and other earths.

In view of what had thus been learned regarding the uraninites of this country it seemed advisable to re-examine the European varieties. Specimens from Przibram, Joachimsthal, and Johannegeorgenstadt contained no rare earths whatever, but they were so contaminated with carbonates and sulphides, and some combination of vanadium, that it seemed for the present useless to attempt an estimation of UO_2 in them. Through Prof. F. W. Clarke, of the U.S. Geological Survey, there were obtained from Prof. A. E. Nordenskiöld specimens marked cleveite from four localities near Moss, Norway, and to Prof. W. C. Brögger are due my thanks for specimens of Blomstrand's original bröggerite, and of the supposed thorium-free uraninite analysed by Lorenzen (*Geol. För. Förh.*, vi., 744), and quoted by Blomstrand (*Journ. Prakt. Chem.*, 1884, xxix., 223 ff.) as a striking proof of the correctness of his view that all varieties of uraninite may be referred to the orthouranate type. These six samples contained, without exception, thoria and other earths, in no case less than 8 per cent, and the four from Prof. Nordenskiöld, with one exception, proved not to be cleveite. Notwithstanding certain variations in composition they were evidently one and the same mineral, just as were those from Branchville and Glastonbury; and the Norwegian and Connecticut varieties, though differing greatly in their relative proportions of UO_2 and UO_3 and in their resistance to the solvent action of acids, were manifestly specifically identical.

These analyses had been practically completed, and a portion of the results very briefly communicated to the public from time to time (*Am. Jour. Sci.*, 1888, [3], xxxvi., 295; *Bull. U.S. Geol. Survey*, No. 60, 1887-1888, p. 131), when, in consequence of a certain observation and its results, an entirely new direction was given to the work and its scope wonderfully broadened. This was the discovery of a hitherto unsuspected element in uraninite, existing in a form of combination not before observed in the mineral world. As already published (*Am. Jour. Sci.*, 1889, [3], xxxviii., 329, where, by a typographical error, UO_2 is made to read NO_2) all tests unite in showing that this element is nitrogen, which is given off in a gaseous form on heating the mineral with a non-oxidising acid, or, as ascertained later, by fusing it with an alkaline carbonate.

It is very unfortunate that this discovery of an escape of gas when treated with an acid, or rather the recognition of its important bearing, for the observation was made at an early date, did not occur sooner; for then more satisfactory results could have been obtained with the—in more than one respect—most valuable material from Branchville, and nearly all the analyses would have been carried out with the most painstaking care, in order to secure the utmost possible accuracy in summation, the importance of which will appear in the sequel. Inasmuch as the analyses were made solely with a view to ascertain the percentages of rare earths and the relative proportions of UO_2 and UO_3 , where a variation of half a per cent, or even more, from the true summation was of very little consequence, that extreme care in the preparation and use of reagents and in analytical manipulation which

* From "Bulletin No. 78, U.S. Geological Survey, 1889-90." An abstract of this paper was published in the *Am. Jour. Sci.*, vol. xl., p. 384.

subsequently acquired knowledge showed to be so necessary was not exercised. Partly in consequence of this, and partly because of the length of time required for these investigations, caused by a want of abundant material, which necessitated oftentimes awaiting the result of one experiment or analysis before venturing upon another, it has been impossible to bring this investigation as far forward as was expected. So much time has elapsed since it was begun, and results of so much importance have been achieved, that it seems advisable to make them public now in detailed form, incomplete as they are in some respects and difficult of interpretation in certain directions.

Before proceeding to discuss the analyses themselves it is necessary to give in some detail the methods of analysis pursued, in order that the degree of credence to be accorded the results may be fairly weighed, and to present the evidence upon which the gas obtained from uraninite has been pronounced nitrogen.

Preparation of Samples for Analysis.

As a prelude to the description of analytical processes employed, the manner of freeing the sample as far as possible from adhering gangue may be briefly described. The specimens consisted, except in the case of the amorphous Colorado, Bohemian, and Saxon varieties, of crystals and crystal fragments more or less coated and invaded by a felspar or mica, or both, sometimes by columbite or a little quartz, and the surfaces opened up by fractures were often more or less coated with a reddish infiltration product which was little, if at all, soluble in the weak nitric acid employed for dissolving the uraninite on commencing an analysis. The sample was reduced to two or three grades of fineness by crushing and passing through several small sieves superposed one upon the other, care being taken to form as little fine dust as possible. When all had passed the coarsest sieve the different fractions were washed by decantation to free from dust, and then carefully panned in watch-glasses of suitable sizes. By this means all the mica and the greater part of the other lighter impurities were removed, and a very fair degree of purification was reached. The columbite, if present, remained mostly with the uraninite, but caused little subsequent trouble. When no more gangue could be panned out without too great loss of material the different portions were united, the specific gravity of the combined sample dried at 100° C. was taken, and it was then finely ground. The fine dust formed in the preliminary crushing was not used, unless for qualitative work, being generally too much contaminated with gangue. The panned material was always examined under the lens when dry, and aside from an occasional adhering reddish fragment appeared clean and free from foreign bodies.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

This Section meets at the Chemical Society's Rooms, Burlington House.

Chairman—T. Tyrer.

Vice-Chairman—W. Crowder.

Committee—C. F. Cross, J. Dewar, A. G. Green, S. Hall, C. W. Heaton, J. Heron, D. Howard, W. Kellner, B. Redwood, W. S. Squire, G. N. Stoker, F. Napier Sutton, Wm. Thorp, T. E. Thorpe.

Communications to be sent to T. Tyrer, Stirling Chemical Works, Abbey Lane, Stratford, E.

Probable Arrangements.

Nov. 2nd, 1891 (Monday):—Mr. W. C. Young, "On Volatile Organic Matter in Potable Water and a Simple Method of Estimating Volatile and Non-Volatile Matter in Water." Dr. S. Rideal, "Some Experiments on Solidifying Petroleum."

Dec. 7th:—Mr. Watson Smith, "A Contribution to our Knowledge of the Soluble and Resinoid Constituents of Bituminous Coals." Dr. Murray Thompson, "The Salt Industry of India."

Jan. 4th, 1892:—Mr. Boverton Redwood, "The Gallician Petroleum Industry."

NOTICES OF BOOKS.

An Elementary Handbook on Potable Water. By FLOYD DAVIS, M.Sc., Ph.D. New York, Boston, Chicago: Silver, Burdett, and Co. London: Gay and Bird. Small 8vo., pp. 118.

THIS book does not by any means cover the same ground as the well-known treatise of Messrs. Wanklyn and Chapman. There are no instructions for the quantitative analysis of water or for its microscopical or bacteriological examination. The nine chapters treat successively of pure water, inorganic constituents, vegetable constituents, animal constituents, micro-organisms, water supplies, natural purification, artificial purification, and systems for central filtration. An appendix enlarges on the "Origin and Home of Cholera," and gives a few rough tests for the recognition of impure waters, such as the permanganate, the silver nitrate, Heisch's sugar test, and Pasteur's microzyme test.

There is here very little to which exception can be taken. Scarcely sufficient justice seems to be done to the action of green chlorophyllaceous vegetation in purifying water by means of the oxygen which it liberates. Nor can it be safely inferred that sewage fungus (*Beggiatoa alba*) is an indication of organic pollution. It is found flourishing luxuriantly in the water of sulphur springs and in the drainage of certain chemical works. The pollution of English streams is painted in a very exaggerated style. Says the author:—"The waters of many where city sewage enters them are actually offensive, and during the summer months, owing to the stench, the passenger traffic is forced to the railways." Polluted waters are not uncommon in England, but we never have met with a place where passenger traffic is "forced to the railways" as above stated.

The purification of polluted rivers as they flow is something more than apparent, as it is proved both by chemical analysis and by observation of the organisms found in the water. The conclusion of the Royal Commissioners given here in a foot-note (or at least of the one Commissioner entitled to form a conclusion) is only in part justifiable. If the English rivers do not purify themselves, it is not a question of their length, but of the volume of sewage in proportion to the river water, and of the constant supplies of pollution which enter every few miles.

What is here said, and very truly said, concerning the inability of the soil to hold back pathogenic bacteria, agrees ill with the methods proposed for supplying cities with water. Such are the ground-water system, or the filtering gallery. It is not often that a well of 40 feet in depth in or near a city is secured by an impervious stratum against the entrance of sewage. The "national system" depends on the use first of precipitants, then, if needed, of filtration, and lastly, of aeration with compressed air under high pressure.

Cholera is traced to the armies of pilgrims frequently traversing India under the most anti-sanitary conditions.

This is perfectly correct; but it should also have been mentioned that pilgrimages from India to Mecca spread the evil westwards, especially as the devotees encounter at the shrine of the prophet other pilgrims from Egypt and the northern coast of Africa. These facts show the folly of expecting to arrest the spread of cholera to Europe by any system of quarantine at Suez. These destructive pilgrimages could be arrested only, if at all, at the cost of a war infinitely worse than the Sepoy mutiny.

Burdett's Hospital Annual and Year Book of Philanthropy, 1891—1892. Containing a Review of the Position and Requirements of the Voluntary Charities, and an Exhaustive Record of Hospital Work. Edited by HENRY C. BURDETT. London: The Hospital (Lim.), 140, Strand, W.C.

THERE is in this volume much which, of necessity, withdraws itself from our view as being economical or political rather than scientific. Such subjects are the policy, and, indeed, the very existence, of the Asylum's Board, the management of different hospitals, and the extent to which such charities are abused by persons well able to pay for private medical attendance. We cannot, however, avoid being painfully struck by the facts that not a few of these institutions are unable to pay their way, and that in many cases beds, and even entire wards, remain unoccupied or closed from the lack of funds. Nor is the amount of disease evidently existing a subject to be passed over lightly. It might probably be a good investment of money and energy if we attended less to the cure of disease and more to its prevention, and if we included in the "preventible" class many affections which are certainly not contagious.

We doubt whether the author has acted advisedly in contrasting the respective conditions and efficiency of the hospitals of Oxford and of Derby, and of holding up the former to censure. We should be apt to think that Derbyshire is far wealthier than Oxfordshire. The proposal to exclude from any share in the proceeds of Hospital Sunday these "Surgical Appliance" or "Aid Societies" which require applicants to canvass for tickets is timely and wholesome.

The canvassing system, indeed! Unless we are misinformed, a "pushing" contemporary has opened a department for the purchase, sale, or exchange of admission tickets.

It is well known that medical establishments which are to all intents and purposes private speculations sometimes figure under the guise of hospitals. Hence the work before us is perfectly justified in suggesting that this should be stopped by law.

The author tells us in his chapter on nurses and nursing that "every boy in his teens wants to be a sailor; every girl in her teens wants to be a nurse." Which of the branches of this dictum is the more exaggerated it would be hard to decide.

A remark is made that "massage has no business to be regarded as a branch of nursing, but unluckily it constantly is." If advertisements are to be believed, proficiency in massage is growing to be required from governesses and lady-helps!

Under the rubric institutions and associations we find mentioned not a few of the most pronounced "anti" type, and having certainly little visible connection with hospitals. Thus we find a "Brown Institute," for the study and treatment of domestic animals, with an income of £1000, a home for stray dogs and cats in receipt of £3000 (!), and two Anti-vivisection Societies, the collective incomes of which reach the total of £2300. On the contrary, the "Society for the Promotion of Medicine by Research" is ignored.

We are very glad to find that the electric quacks, now so thriving, do not here figure in the character of philanthropists.

CORRESPONDENCE.

THE CONSTITUTION OF BUTTER, &c.

To the Editor of the Chemical News.

SIR,—In his letter (CHEMICAL NEWS, vol. lxiii., p. 201) Mr. Wanklyn takes exception to my statement that "Messrs. Wanklyn and Fox have never published a single original experiment in support of their assertion that the proportion of glycerin yielded by saponification of butter and other fats exhibits any grave departure from the amount required by the accepted view of their constitution."

Notwithstanding Mr. Wanklyn's denial, the above statement is, I believe, perfectly correct as it stands. If I had stated that "neither Mr. Wanklyn nor Mr. Fox had ever published" I should have been in error. Mr. Fox has not published anything of the kind to my recollection, and it is only fair to say that he has taken no share in Mr. Wanklyn's recent resuscitation of the isoglyceride theory. But Mr. Wanklyn did describe, in a paper read by him before the Society of Chemical Industry in January last (*Journal*, x., 89), a single experiment which he had made in 1883, but had not previously published.

I am sorry that Mr. Wanklyn did not remind me of this one solitary experiment when I made the statement, to which he now takes exception, in his presence some months since. It was certainly with no intention of inadequately stating Mr. Wanklyn's case that I omitted to mention the matter in my paper printed on page 179. At the meeting of the Society of Chemical Industry at which Mr. Wanklyn read his paper the experiment was very strongly criticised, as being badly devised and inconclusive in several respects, and Mr. Wanklyn made no sufficient answer to the objections then raised. Mr. Wanklyn's detailed account of the experiment, as printed in the *Journal of the Society of Chemical Industry*, contains abundant internal evidence of the—to put it mildly—inconclusive nature of the experiment, as I am quite prepared to show if required. I am therefore somewhat surprised that Mr. Wanklyn still lays stress on the experiment, and regards it as lending support to his theory. The result is absolutely inconsistent with the more recent experience of various independent observers, and Mr. Wanklyn would have been wise to allow the record of the experiment to remain in his note-book, where he had already let it rest for seven or eight years.

Since the appearance of Mr. Wanklyn's letter I have attempted to repeat his experiment of heating slaked lime with butter-fat, but have met with a practical difficulty in which I shall be glad of his advice. Mr. Wanklyn kept the mixture on the water-bath for a "long period," stirring constantly. My experiment has now continued for nearly forty hours, and my stirring powers are exhausted; in fact, they long since degenerated from "constant" to "frequent," and from that to "occasional." Under these circumstances I started a fresh quantity in a closed flask in the water-oven. This flask has been frequently shaken during several days, but there is no apparent sign of saponification having taken place. It appears still to be simply melted butter, with slaked lime in suspension. How long did Mr. Wanklyn's constant stirring continue? Where am I wrong, and when am I to regard the saponification as complete?

Dr. William Johnston writes:—"Mr. Allen charges me with having stated that tallow required 23 per cent of caustic potash (KHO) for its saponification, against 19.3—19.8 per cent as the united experience of other observers. I never said or wrote anything of the kind; the statement is purely a misrepresentation." This is rather a strong denial, and somewhat more positive than the facts warrant. What I stated (page 182) was that Dr. Johnston had "recently published experiments

(*Analyst*, xvi., 26) according to which tallow requires 23 per cent of caustic potash, &c." For "tallow" read "beef fat," which is practically synonymous, and my statement is absolutely correct; and seeing that the united experience of other observers is that "beef fat," equally with tallow, requires from 19.3 to 19.8 per cent of potash for its saponification, Dr. Johnstone's experience that 23 per cent is required is almost as unaccountable as his correction was unfair and unnecessary. Dr. Johnstone's position is similar to that of a man who has stated that he was born in 1868, and then objects to others holding that his age is now twenty-three.

Dr. Johnstone's reference to Mangold's recent results, and his claim that they furnish "an unexpected confirmation" of his own statements, have already been dealt with by Mr. Hehner. Whether or not butyric acid is oxidised to oxalic acid under exceptional conditions is beside the question. Mangold's results, like my own experiments, absolutely contradict Dr. Johnstone's statement that Benedikt and Zsigmondy's process for determining glycerin by oxidation to oxalic acid by alkaline permanganate is rendered inaccurate by the presence of butyric acid. Neither does Mangold in any way endorse the "eccentric equation" $C_4H_8O_2 + O_6 = 2C_2H_2O_4 + H_4$, according to which Dr. Johnstone appears to hold that free hydrogen is evolved in presence of excess of alkaline permanganate.

The other remarks of Dr. Johnstone scarcely call for comment. As the estimation of glycerin by bichromate, which I quoted as having yielded 11.83 per cent on the butter, was made on an acidulated liquid which had already been distilled to a small bulk, the "volatile fatty acid which readily reduces acid bichromate" could scarcely have interfered. No one contends that the oxidation processes of estimating glycerin are reliable in all cases—in fact, I have stated exactly the opposite.

Similarly, no one doubts that, under very extreme conditions chromic acid, and possibly alkaline permanganate, will oxidise butyric to carbonic acid; but that is not the point at issue.—I am, &c.,

ALFRED H. ALLEN.

Sheffield, October 24, 1891.

BEHAVIOUR OF BUTYRIC ACID WITH ALKALINE PERMANGANATE.

To the Editor of the Chemical News.

SIR,—In reply to your correspondent, Mr. Otto Hehner (*Chemical News*, vol. lxiv., p. 212), I decline the compliment and the reproach as well as his literal translation, and beg to inform him that I quoted from an English translation of Mr. Mangold's paper, made by a German whose knowledge of the English language is infinitely superior to that of your correspondent's, and is as follows:—Mangold, speaking of his modification of Benedikt and Zsigmondy's method, says "The presence of butyric acid does not affect the result, since butyric acid does not become oxidised in the cold by an alkaline solution of permanganate; butyric acid yields oxalic only when boiled for a considerable time with an excess of alkali and potassium permanganate."

Mangold's experiments are made upon pure glycerin, and not upon the soluble products of a saponification; but why does Mangold use cold alkaline permanganate if oxalic acid is not produced? However, Mr. Hehner in his literal translation admits that "the amount of oxalic acid is either not increased at all in the presence of butyric acid, or only very slightly." Exactly, and by prolonged boiling one can obtain the theoretical quantity. If the fact "was not carefully suppressed to my disadvantage," it certainly at all events was not suppressed to my advantage, as time will tell.—I am, &c.,

WILLIAM JOHNSTONE.

15, Fish Street Hill,
October 24, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 15, October 12, 1891.

Variation of the Composition of Jerusalem Artichokes at different Stages of their Vegetation. The part played by the Leaves.—G. Lechartier.—The author determines the composition of these plants in September when they have already reached their normal growth, and when the tubers exist only in small proportions. The leaves wither and die from the moment when they do not contain a sufficient quantity of phosphoric acid or of potassa. The minimum quantities per kilo. of dried vegetable matter are—Phosphoric acid 3.48 to 4.10 grms., potassa 3.18 to 3.36.

Circulation of the Specific Heat of Liquids.—G. Hinrichs.—The molecular specific heat of liquids at any given temperature is determined by the minimal momentum of inertia of the molecule, i.e., the molecules revolve on the natural axis the momentum of inertia of which is the smallest.

Fusion-Point of Certain Binary Organic Systems.

—Leo Vignon.—In all the cases examined the melting-points observed differ from the melting-points calculated. If we represent graphically the melting-points observed with reference to the variations in weight of one of the bodies composing the mixture, we have two possible cases. (a) The melting-points observed differ greatly from those calculated and are lower. For certain proportions of the components the mixture melts below the melting-point of the most fusible body. (b) The melting-points observed differ little from those calculated and are rather higher. The chemical functions of the bodies in question do not seem to affect these results.

Calorimetric Researches on the Condition of Silicon and Aluminium in Cast-Irons.—F. Osmond.

Silicon may combine with iron with disengagement of heat; but the compound formed is dissociated by an excess of iron, and subsists only if the presence of silicon in the compound is sufficient. Aluminium, in the conditions in which it is used in siderurgy, dissolves in melted iron with absorption of heat. If the reverse phenomenon is observed, as manufacturers maintain, the liberation of heat cannot be ascribed to an exothermic combination of aluminium with iron, but only to the reduction by aluminium of the dissolved iron oxide, and probably to an allotropic modification of the iron.

Formation-Heat of Platinic Bromide and of its Principal Compounds.—Léon Pigeon.—Not adapted for useful abstraction.

Zeitschrift für Analytische Chemie.
Vol. xxx., Part 3.

Separation of Cobalt and Nickel by the Nitrite Method.—M. Baubigny (*Annal. de Chimie et de Phys.*).

—This method, first proposed by N. W. Fischer, is known to be excellent. It is, however, as Künzel and Erdmann have shown, not available if barium, strontium, or calcium is present, since, in this case, along with the potassium-cobalt nitrite, there is thrown down a compound of this salt with barium, strontium, or calcium nitrite. Baubigny now calls attention to a further nitrite which contains lead, nickel (nickelous oxide), and potassium. As lead salts in many respects are approximate to the barium salts it seemed to the author probable that the former would behave similarly with potassium nickelous nitrite. This conjecture was confirmed by the following experiment:—If to a solution of potassium nitrite mixed with

nickelous acetate or nitrate there is further added only a small quantity of lead acetate or nitrate, we obtain an orange-yellow precipitate. This precipitate in appearance resembles cobalt-potassium nitrite, and is very sparingly soluble even in water acidulated with acetic acid. On qualitative examination there are found in the compound nitrous acid, lead oxide, nickelous oxide, and potassa. The presence of lead compounds, therefore, like that of the alkaline earths, excludes the use of the nitrite method for the separation of cobalt and nickel. This source of error depending on the presence of lead compounds is of the greater importance, as the alkaline nitrites are generally obtained by treating the corresponding nitrates with metallic lead, and hence often contain a small quantity of lead oxide. The nitrite to be used for the separation of cobalt and nickel must therefore always be tested for lead and purified if this metal is present. Not only cobalt and nickel, but copper, give a precipitate under the above conditions; in presence of zinc and cadmium no insoluble compounds are formed.

Solubility of Thallous Iodide and Determination of Thallium.—J. H. Long.—(From the *Journal of Analytical Chemistry*).

Determination of Cuprous Oxide in Metallic Copper by Hampe's Method.—Notes by C. Rammelsberg (*Ber. Deutsch. Chem. Gesell.*), Hampe (*Zeitschr. Anal. Chem.*, xvii., 127), and F. P. Dewey (*Journal of Anal. Chemistry*). It appears that on treating metallic copper with a neutral solution of silver nitrate in excess at common temperatures, all the cuprous oxide present is converted into insoluble basic nitrate, $Cu_4H_6N_2O_{12}$.

Analysis of a Mixture of Silver Chloride, Cyanide, Sulphocyanide, Ferriocyanide, and Ferrocyanide.—Jules Teissier (*Bulletin de la Soc. Chimique de Paris*).—This paper will be inserted in full.

Titanium Carbide in Crude Iron.—P. W. Shimer (*Journal of Analytical Chemistry*).—The author determines titanium in irons by the following methods:—1. The residue insoluble in dilute hydrochloric acid is fused with potassium bisulphate, and the titanate acid is separated in the known manner. 2. The residue insoluble in dilute hydrochloric acid is treated with nitric acid in order to bring the titanium into solution; the nitric solution is precipitated with ammonia, the precipitate is filtered off, washed, and again dissolved in dilute sulphuric acid. After the excess of sulphuric acid has been neutralised, and the solution mixed with some sulphurous acid, the titanate acid is thrown down by prolonged boiling. The precipitate is filtered, washed, and melted with sodium carbonate. The melt, after extraction with water, yields insoluble sodium titanate, which is dissolved in sulphuric acid, and the titanate acid is finally separated from the solution. 3. The iron in the state of turnings is heated to redness in a current of dry chlorine, and the titanium chloride volatilised is received in water in a series of flasks and tubes. Of these three methods it appears that the first is preferable.

Action of Organic Compounds upon the Alkaline Sulphohydrates.—F. Fuchs (*Monatshäfte*).—Already inserted.

The Recognition of Diresorcine in Synthetic Phloroglucine.—J. Herzig and S. Zeisel (*Monatshäfte für Chemie*).—Already inserted.

The Losses of Nitrogen in the Analysis of Guanidine and Biguanidine Compounds according to the Will-Varietrapp Method.—J. Freydl (*Monatshäfte für Chemie*).—The author concludes that the loss of nitrogen is chiefly due to the combustion of the nitrogen formed, and that the production of cyanides has scarcely an appreciable effect.

Determination of Citric and Malic Acid in Fruits.—Edo Claassen (*Pharm. Rundsch. und Chemiker Zeitung*). The crushed fruits are stirred up with hot water, filtered, and the filtrate is mixed with milk of lime in slight

excess. The liquid is acidulated with hydrochloric acid, filtered, the precipitate gently heated with an excess of ammonia until the flocculent matter which is separated out has subsided. It is then filtered off, the filtrate is evaporated to dryness, and the residue is taken up with boiling water with an addition of ammonia. The precipitate of calcium citrate is filtered off on a weighed filter and washed with hot water. The filtrate and the washings are evaporated to dryness in the same manner, and thus small quantities of calcium citrate are recovered which have become dissolved. For the determination of malic acid the crushed fruit is treated with hot water, filtered, and the filtrate is mixed with ammonia in slight excess. It is filtered again, the filtrate evaporated to dryness, and the residue finely pulverised is mixed with absolute alcohol containing ammonia. After standing for 24 hours it is filtered again, washed with absolute alcohol, and the filtrate is precipitated with an exactly sufficient quantity of an alcoholic solution of lead acetate. The precipitate of lead malate is collected on a weighed filter which has been dried at 100°, washed with alcohol, dried at 110°, and weighed. The malic acid is found on multiplying the weight of lead malate by 0.2925.

Determination of Tannin.—A number of notes from the *Journal de Pharmacie et de Chimie*, the *Chemiker Zeitung*, the *CHEMICAL NEWS*, the *Analyst*, *Dingler's Journal*, and the *Moniteur Scientifique*, some of which will be specially noticed by opportunity. H. M. Raer criticises in the *Journal of the American Chemical Society* the various methods for the determination of tannin. He pronounces the methods of Loewenthal and Hammer as the only useful procedures, and in these he points out certain defects.

Examination of Water; Determination of Iron.—A. F. Jolles (*Archiv. für Hygiene*).—A colorimetric process depending on the use of ammonium sulphocyanide.

Determination of Oxygen dissolved in Water.—H. E. Roscoe and Joseph Lunt (*Ber. Deutsch. Chem. Gesell.*).—The authors point out the defects of Schützenberger's process, and propose a new apparatus by which these faults may be avoided.

Determination of Nitric Acid in Water.—G. Loof (*Pharm. Central Halle*).—The author dissolves 2 centigrams of sodium salicylate in 5 c.c. of the water in question and adds 10 c.c. of colourless sulphuric acid, so that it may flow slowly down the side of the glass, forming 2 strata of liquid. The 2 strata are then mixed by shaking the glass, and if nitric acid is present the entire liquid takes a colour which varies from red to pale yellow, according to the proportion of the acid; 1 part of nitric acid may thus be detected in 100,000 parts of water. F. Musset states in the same paper that on testing water for nitrous acid by means of zinc iodide and starch solution with acetic acid, the reaction produced becomes continually darker and darker. This change is due to the reducing action of bacteria upon the nitrates present.

Determination of Nitric Acid.—E. Schmidt (*Apoth. Zeit.*).—This paper cannot be intelligibly reproduced without the accompanying cut.

Determination of Organic Nitrogen in Natural Waters.—T. M. Drown and H. Martin.—The authors apply the Kjeldahl process.

Colorimetric Determination of Ammonia.—Max Müller.—From the *Zeit. f. Angew. Chem.* No particulars are given.

Determination of Organic Matter in Water.—Joseph Klein (*Archiv. der Pharm.*).—A modification of the Schulze-Trommsdorff method.

Detection of Spurious Mace.—Hefelmann (*Pharm. Zeit.*).—The suspected sample is extracted with boiling alcohol and the extract filtered. If the sample is pure the filter takes up merely a faint yellow colour, but if so-called Bombay mace is present the filter is coloured red at its margin.

MISCELLANEOUS.

Edward Riley and Co.—Mr. E. Riley, F.C.S., who has been in practice as a metallurgical chemist and mineral analyst during the past thirty-seven years, has now associated himself with a duly qualified and experienced mining engineer, Mr. Frank Merricks, Associate Royal School of Mines, &c., also an experienced analyst and metallurgist. Mr. W. H. Herdsman, who has been associated with Mr. Riley for the past twenty years, and has had considerable mining and metallurgical experience in all parts of Europe, will assume the management of this branch of the business, and will assist in carrying on the metallurgical and analytical business as heretofore. A branch office will be opened immediately in Cordova, Spain, under the charge of Mr. Merricks. The firm will be prepared to undertake the inspection of mining properties of all kinds in Spain or elsewhere, and to advise and superintend prospecting work, and all smelting, refining, and other metallurgical operations.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Laboratory without Gas.—Would any chemist who has practical experience on the subject oblige by informing me as to the best means of carrying on the work of a small laboratory in a district where there is no gas?—F.L.C.

Manufacture of Soap.—Will you oblige one of your subscribers by letting me know what are the latest books treating of manufacture of soap in England, with the name and address of the publishers?—H. MANBERT.

[The following books may be consulted on the manufacture of soap:—"On the Manufacture of Soaps," by C. Morit (1871); Trübner and Co., London. "Soaps and Candles," by James Cameron (1888); J. and A. Churchill, London. "Soap, and its Lubricants, and Glycerin," by W. L. Carpenter (1893); E. and F. N. Spon, London. "The Art of Soap-making," by A. Watt (1885); Crosby Lockwood and Co., London.—Ed. C. N.]

MEETINGS FOR THE WEEK.

MONDAY, NOV. 2nd.—Royal Institution, 5. General Monthly Meeting.

THURSDAY, 5th.—Chemical, 8.

FRIDAY, 6th.—Physical, 5. "On Corresponding Temperatures Pressures, and Volumes," by Prof. Sydney Young.

ERRATUM.—P. 204, col. 2, line 26 from bottom, for "Analyst, October, 1891," read "Analyst, September, 1891, p. 169."

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THE CHEMICAL NEWS.

VOL. LXIV., No. 1667.

ELECTROLYTIC DETERMINATION OF METALS AS AMALGAMS.*

By G. VORTMANN.

IN the determination of metals by the electrolysis of their solutions it is essential in the first place for the metal to be separated out quantitatively as such or in the state of a known compound, and secondly that the precipitate obtained forms a uniform coating on the platinum capsule used as an electrode, and adheres so firmly that no loss takes place on rinsing with water and alcohol and undergoes no change during drying. Among the metals which have been hitherto determined electrolytically iron, cobalt, nickel, zinc, cadmium, bismuth, copper, mercury, silver, gold, platinum, tin, and antimony have been separated as metals, but manganese and lead as peroxides. Some of the metals above-mentioned present difficulties in electrolysis, as they form a uniform adhesive stratum only if present in small quantities, such as antimony, bismuth, cadmium, lead, and manganese. The idea of obtaining a uniform adhesive coating by the addition of such metals as are apt to be deposited as spongy masses seems first to have presented itself to C. Luckow, who in 1880 observed the formation of amalgams on the simultaneous deposition of mercury and of other metals. In 1885 he gave directions for obtaining zinc as an amalgam, and recommended an addition of mercury for the separation of silver from the solution of its nitrate. Before Luckow, W. Gibbs (1883) recommended to place a weighed quantity of mercury upon the bottom of the beaker containing the solution of the metal connecting it with the negative pole of the battery. The quantity of the metal deposited was to be concluded from the increase in the weight of the mercury. Gibbs employed this method for the determination of mercury, cobalt, and tin, and regarded it as probably not applicable to antimony and arsenic. Strictly speaking, he merely intended to use mercury as a negative electrode in place of the platinum capsule.

In view of the practical importance and the convenience of the electrolytic methods, I considered it advisable to attempt the separation of all those metals in the form of amalgams which have hitherto been electrolytically determinable only with especial precautions. I used the mercury not in the metallic state, but preferred mercury chloride, which is more easily weighed and obtained in a pure condition, or, in its place, in the electrolysis of acid solutions I used pure mercuric oxide obtained by precipitation. In the simultaneous separation of mercury along with the metal to be determined, the amalgam is more uniformly deposited than if metallic mercury had been used. The precipitability of mercury from all its solutions much assists the determination of metals as amalgams. It is sufficiently known that it can be readily deposited from acid solutions, from its solution in potassium cyanide, and from the solution of the double sodium pyrophosphate after the addition of ammonia or ammonium carbonate. It may also be easily separated from the solution of the double ammonium oxalate, from the solution of its salts in potassium iodide, in sodium sulphide, or in ammonia in presence of tartaric acid.

All the precipitates after the completion of the electrolysis were washed first with water, then with alcohol, and lastly with ether, dried, and gently blowing upon it, whilst the capsule is gently warmed by holding it in the

palm of the hand and finally placing it in the desiccator. It is not necessary to weigh the amalgams forthwith, as no loss takes place by volatilisation of mercury if the capsule is left for days in the desiccator or even in the open air.

The strength of the current the author regulated entirely according to the progress of the analysis. At the beginning of the electrolysis a current was passed for some minutes, giving 6—8 c.c. detonating gas per minute; as soon as the metals began to be separated the current was reduced to 2—3 c.c. of gas per minute, and again strengthened gradually, so that the analysis was generally completed with a current giving 6—8 c.c. of detonating gas per minute.

Determination of Mercury.

1. *Separation of Mercury from the Solution of Ammonium Oxalate.*—If a solution of mercuric chloride is mixed with ammonium oxalate in excess it remains clear, and on electrolysis the mercury is readily separated. This method, like the separation of mercuric chloride from an acid solution, has the defect that a thin film of calomel is formed on the surface of the liquid, which is reduced only after a long time.

2. *Separation of Mercury from an Ammoniacal Solution.*—The solution of mercuric chloride in water is mixed with tartaric acid, ammonia in excess is then added, and the liquid is then electrolysed. The mercury separates well and quickly by this process: ammonium sulphide is used to ascertain if the precipitation is complete.

3. *Separation of Mercury from a Solution of Sodium Sulphide.*—Mercuric chloride is dissolved in water and mixed with a solution of sodium hydroxide containing sodium sulphide until the precipitate first formed is completely re-dissolved. The liquid is then diluted with water and the electric current is passed through. The solution of the mercurial salt in sodium sulphide is not always clear; sometimes a slight turbidity is perceptible, probably due to finely-divided metallic mercury, but which does not interfere with the electrolysis. The separation of the mercury ensues easily and completely, and it is at an end when a specimen of the solution remains clear on adding ammonium chloride. At the commencement of the electrolysis the positive electrode becomes overcast with a black film of mercury sulphide which gradually disappears again. As a rule the separation of mercury is complete when the positive electrode is covered with a yellow layer of sulphur and the black film has disappeared.

The mercury separated from the solution of sodium sulphide coats the capsule uniformly as a reflective layer, consisting in part of minute drops.

4. *Separation of Mercury from Solution of Potassium Iodide.*—On the electrolysis of a solution of mercuric chloride in an excess of potassium iodide the mercury separates easily and uniformly, whilst iodine is liberated at the positive pole and finally floats on the surface of the liquid in the form of a cellulose clot. If a specimen of the liquid after being decolorised with sodium sulphide is not coloured brown on the addition of ammonium sulphide all the mercury has been separated out.

A few c.c. of concentrated soda-lye is then poured into the capsule without interrupting the current, the liquid is mixed by moving the positive electrode up and down until the iodine is completely dissolved, and the current, slightly strengthened, is passed through the liquid for an hour in order to re-precipitate any traces of mercury which have been re-dissolved by contact with the solid iodine. If a sample of the solution on the addition of ammonium sulphide gives a pure white milky precipitate, the alkaline liquid is poured off, and the mercury is washed in the manner described above. If the quantity of iodine liberated is small, the iodiferous solution is poured off and the mercury quickly washed first with solution of sodium sulphite and then with water, alcohol, and ether.

The solution of the mercuric chloride can be mixed to

any extent with soda- or potassa-lye without causing a precipitate. From such an alkaline solution the mercury may be readily deposited electrolytically and washed with pure water only, as on rinsing with alcohol, small quantities pass into solution in the state of a grey film. E. F. Smith has observed a similar fact in mercury separated from a solution of potassium cyanide.

The mercury precipitated electrolytically in any manner is permanent in the air and undergoes no change on remaining 15 hours in the desiccator.

(To be continued).

ELECTROLYTIC SEPARATIONS.

By EDGAR F. SMITH and F. MUHR.

As it appeared from the author's former experiments (*Amer. Chem. Jour.*, xii., p. 252) that gold can be completely precipitated by the electric current from its double cyanides, the author attempted to decide what metals can be separated from gold in this manner. Former experiments had showed that in a current of 1-100th ampère requires 36 hours to separate palladium from a solution containing potassium cyanide in excess. This behaviour indicated the possibility of separating gold from palladium, and the two metals were therefore submitted to the current under the following condition:—0.1162 grm. gold and 0.1200 grm. palladium dissolved in 1½ grms. potassium cyanide and made up to 150 c.c. were treated with a current giving off 0.8 c.c. of detonating gas per minute. The quantity of gold obtained was 0.1162 grm. The separation of the gold required 12—14 hours. Water both cold and warm was used for washing the precipitated metal, and the deposits were produced at once in the platinum capsules.

The gold was then dissolved by pouring a dilute solution of potassium cyanide into the platinum vessels and separated by connecting the latter with the anode of a weak battery.

The solution of gold cyanide was decomposed by aqua regia, and the gold chloride obtained was carefully tested for palladium. But no palladium was discovered.

Gold from Copper.—This separation was found successful. 0.1725 grm. gold and 0.1250 grm. copper dissolved in 1½ grms. potassium cyanide and made up to 150 c.c. were submitted for 12—14 hours to a current giving off 0.8 c.c. detonating gas per minute. The quantity of gold obtained was 0.1725 grm., and no copper was found in the deposit.

Gold from Cobalt.—The quantities taken for the experiment were 0.1792 grm. gold and 0.15—0.20 cobalt were dissolved in 3 grms. potassium cyanide, diluted to 150 c.c., and treated with a current giving only 0.6 c.c. gas per minute. The gold found was 0.1789 grm.

Gold and Nickel.—The quantities taken were gold 0.1725 grm., nickel 0.1373 grm. in potassium cyanide, made up to 150 c.c. and submitted to a current of 0.5 c.c. per minute. The gold extracted was 0.1724 grm.

The electrolytic separation of zinc from mercury, cadmium, and silver, in a solution of potassium cyanide, was effected without difficulty, but the current must yield at least 2—3 c.c. of detonating gas per minute.

Gold from Zinc.—The quantities taken were 0.1792 grm. gold, 0.2 zinc, potassium cyanide 3 grms., made up to 150 c.c. and treated with a current giving 0.5 c.c. of detonating gas per minute. The amount of gold found was 0.1796 grm. The battery used consisted of 6—10 "crow-foot cells." The poles during the precipitation of the metals were at a distance of 1½ inches from each other. The solutions were covered with watch-glasses to prevent loss and exclude dust. The precipitation of the metal is completed as soon as the surface of a sheet of platinum freshly introduced remains unaltered.

Gold from Platinum.—For this separation a more

powerful current was used. The quantities taken were 0.1467 grm. gold, 0.2433 grm. platinum, in potassium cyanide 2½ grms., made up to 150 c.c. The current gave off 1 c.c. detonating gas per minute. The gold obtained was 0.1474 grm.

Silver from Platinum.—The metals were dissolved in an excess of potassium cyanide, and the solution was directly electrolysed, using a current of the same strength as that in the last experiment. The silver was deposited free from platinum.

Cadmium from Platinum.—The cadmium precipitated was never free from platinum.

Mercury from Platinum.—This separation is easily effected. For quantities of mercury 0.1902 grm., and platinum 0.2433, a current was used giving off only 0.2 c.c. of gas per minute. The mercury found was 0.190 grm. The separations of gold, silver, and mercury from platinum were effected in the cold.—*Ber. Dent. Chem. Gesell.*, vol. xxiv., p. 2175.

DETERMINATION OF SMALL QUANTITIES OF ALKALI AND RECOGNITION OF THE NEUTRALITY OF WATER.

By F. MYLIUS and F. FOERSTER.

A CERTAIN conclusion as to the insolubility of glass vessels in aqueous liquids has been hitherto involved in considerable difficulties, as the only available means has been a determination of the loss of weight which the vessels underwent on being heated with such liquids. We have sought to determine the permanence of glasses by the direct determination of the quantity of alkali dissolved out of them by water. It was evident that, in order to obtain more precise results, the gravimetric method must be superseded by a volumetric procedure. The necessary increase of the sensitiveness of alkali-methods has been attained by means of a special indicator (iodeosine), which one of us had already proposed for the comparative examination of the surfaces of glasses.

Each of the colouring-matters used in volumetric analysis as indicators has a special value, and is adapted to a given purpose. The sensitiveness of indicators is in every case limited, a titration with very dilute solutions the change of colour is only effected gradually. The cause of this lies especially in the hydrolytic scission to which the salts of tinctorial acids are liable in dilute solutions. Hence near the neutral point the colour of the free tinctorial acid appears along with the colour of the salt when the acid is coloured, or if it is colourless the colour of the salt fades away, but in neither case do we encounter an abrupt change of colour. For the titration of dilute solutions such indicators are preferable as, like the strong acids, form the most permanent alkaline salts. Titration with them is little affected by the presence of carbonic acid, since, being powerful acids, they easily expel carbonic acid from carbonates.

Among the artificial colours which have recently come into use these properties seem to a great degree characteristic of the eosines, as their halogenous power probably depends on their high proportion of halogen. Their fundamental substance, fluoresceine, as also ordinary eosine, has been introduced into volumetric practice. Our experiments have shown that iodeosine, or erythrosine, is especially adapted for the determination of small quantities, but under peculiar conditions, which render a preliminary investigation of its properties necessary.

Iodeosine, or erythrosine, has the composition $\text{C}_{20}\text{H}_{11}\text{I}_2\text{O}_5$; it is a commercial product, and is especially used in cotton-dyeing and paper-staining.

The pigment, as supplied by the Baden Aniline Works is a brick-red powder, soluble without fluorescence, but

with a rose-colour in dilute alkalis. From this solution it is re-precipitated by supersaturation with acid. The commercial preparation contains as impurity small quantities of matters almost insoluble in ether and in dilute solution of pyridine. The alkaline solution of these impurities has a violet-blue tone. For its purification the commercial substance was dissolved in aqueous ether, and removed from the filtered solution by shaking out with a dilute soda-lye; from the alkaline solution the brick-red sodium salt is precipitated by a stronger soda-lye. The salt is filtered, washed with spirit, and re-crystallised from hot alcohol. As the solution cools it is obtained in well-developed, almost rectangular tables, with a green surface colour, whilst the impurities remain in the mother-liquor.

Pure iodeosine has a decidedly lighter colour than the commercial product; it is almost insoluble in absolute ether, benzene, petroleum ether, chloroform; more readily soluble in acetone, in alcohol, and in aqueous ether. In aqueous alkali the purified colouring-matter dissolves, as it might be expected, with a more yellowish tone than the crude product. Supersaturated solutions can be obtained by shaking up the recently precipitated amorphous colouring-matter with ether. If the solution is allowed to stand, the excess of colour is deposited in small orange crystals of a rhombic form.

Iodeosine has not hitherto been employed in alkalimetry; if it is used in the ordinary manner it behaves as a bad indicator. If to an alkaline solution we add a trace of iodeosine, and neutralise with normal hydrochloric acid, the change from rose to orange takes place with undesirable tartness, and a decided excess of acid is necessary to complete the reaction. The use of this colour as an indicator is possible only if the titration is effected in presence of ether in a shaking vessel. The neutral point can then be distinguished very sharply, as the slightest excess of acid on shaking causes the trace of eosine present to pass from the aqueous into the ethereal stratum. The aqueous liquid then appears colourless.

Titration with Mille-Normal Solutions.

In the determination of large quantities of alkali, effected with normal and decinormal solutions, there is no cause to make use of the process just mentioned, the employment of the ordinary indicators in aqueous solutions being then more convenient. In the ordinary manner we may, as is well known, effect titrations with centinormal solutions with some accuracy. But this is the limit. By means of iodeosine and ether it is possible to effect titrations with mille-normal solutions with the greatest distinctness.

(To be continued.)

PROPERTIES OF PRECIPITATES, &c.*

By E. WALLER, Ph.D.

(Continued from p. 220).

$Fe_2(OH)_6$.

Rem.—Precipitation in most cases effected by NH_4OH .

When but little ferrous iron is present and heat is applied, a finely-divided red ("brick-dust") precipitate separates, which is insoluble except in concentrated HCl.

In presence of a larger proportion of ferrous salt, black $Fe_3(OH)_8 = Fe(OH)_2, Fe_2(OH)_6$ will separate. With more ferrous salt the precipitate is green, the colour being lighter the larger the proportion of ferrous salt; and when the iron is all absolutely in the ferrous form, the precipitate is white. Whenever ferrous salt is present, a double ammonium ferrous salt forms, which remains in solution, from which the iron slowly precipitates by

absorption of oxygen and conversion to the ferric form. NH_4Cl favours the precipitation of $Fe_2(OH)_6$.

Cond.—Iron should be in ferric form. H_2S should be absent.

Sol.—Soluble in acids and in solution containing citric, tartaric acids, &c., as well as other organic substances, glycerin, sugar, &c. Insoluble in alkalis.

Contam.—Basic ferric salts, especially basic sulphate, unless the precipitant is in moderate excess. When precipitated by fixed alkalis the precipitate contains some alkali, which is washed out with great difficulty. Precipitate will carry with it phosphoric acid as $Fe_2(PO_4)_2$ in nearly sufficient quantity to form that compound. The excess of phosphoric acid will remain in solution unless some other base (Al, Ca, &c.) is present to carry it down in combination. Precipitate may also contain nearly, if not quite, all of the Al, Mn, and silica present. Mg, Co, Ni, Zn, and Cu are also liable to be present in the precipitate, Ca also as $CaCO_3$ if the alkaline solution has absorbed any CO_2 from the atmosphere. From these latter (Mg, &c., including Ca), the precipitate may be freed by one or more re-solutions and re-precipitations.

Ign.—Converted to Fe_2O_3 . With C, a partial reduction to Fe_3O_4 may occur. Fe_2O_3 is restored by adding a few drops of HNO_3 , and re-ignition. In contact with NH_4Cl , may form volatile Fe_2Cl_6 .

$Fe_2(OH)_n(C_2H_3O_2)_{6-n}$. Basic Ferric Acetate.

Rem.—Ferrous salts, if present, are not precipitated. If in very small proportion, they may induce the formation of the "brick-dust" precipitate alluded to under $Fe_2(OH)_6$. In analysis of iron ores and manufactured irons, the reduction of the major part of the iron to the ferrous form and application of the basic acetate, separation is frequently resorted to in order to remove the excess of iron before determining phosphorus.

Cond.—The dilute solution should contain but little free acetic acid. The (ferric) iron should be in the form of acetate. This is obtained by neutralising the free mineral acid present and adding $NaC_2H_3O_2$. No precipitate should appear in the cold, but on boiling a few minutes (three to five) it separates completely, provided not too much free acetic acid is present. Too long boiling causes the precipitate to assume a form which filters with some difficulty.

Sol.—Soluble in cold dilute acetic acid and in mineral acids, also in citrates and other organic substances mentioned as solvents of $Fe_2(OH)_6$. Insoluble in hot acetic acid only when quite dilute.

Contam.—Salts of fixed alkalis. Silica, alumina salts, and P_2O_5 —the latter in the form of $Fe_2(PO_4)_2$ [see $Fe_2(OH)_6$]. The precipitate may also contain some Mn, Zn, Ni, Co, or Cu. Mn is more likely to be present if the amount of $NaC_2H_3O_2$ added was large. The amounts of these last in the precipitate is much diminished by increasing the proportion of free acetic acid in the solution. The danger of having sufficient free acid to prevent the precipitation of all the iron is, however, considerable. By re-dissolving in HCl, neutralising, adding $NaC_2H_3O_2$ and re-precipitating, the Zn, Ni, &c., can be removed. Zn usually gives the most trouble. If much is present, it may be advisable to precipitate in a solution containing enough free (acetic) acid to hold a little Fe in solution. The later may be separated by evaporating the excess of acid from the filtrate. SiO_2 and Cu should be previously removed by known methods, if their presence in the precipitate will influence subsequent work.

When chromium is present in the solution the action is peculiar. When iron predominates decidedly, all of the chromium is precipitated with it. If the ratio of chromium to iron is nearly the same, not only much of the chromium, but some of the iron is retained in the solution.

$Al_2(OH)_6$.

Rem.—In general terms the precipitate is very similar to $Fe_2(OH)_6$, but is more easily prevented from forming,

* From School of Mines Quarterly, xii., No. 3.

and when separated, being more gelatinous in character, is less readily managed. Usual precipitate ammonia. A good method of managing consists in rendering slightly alkaline with ammonia, and passing H_2S , raising the temperature at the same time gradually to boiling.

Cond.—Neutral or slightly alkaline solution, containing preferably NH_4Cl .

Sol.—Dissolves in acids and in fixed caustic alkalis; somewhat soluble in ammonia, especially in the cold. From this solution it may be separated by boiling out the major part of the NH_3 , particularly if NH_4Cl is present. Precipitation prevented by presence of tartrates, citrates, sugar, glycerin, &c. After boiling or standing for a short time the precipitate will dissolve in acids (even HCl) slowly and with some difficulty.

Contam.—Basic Al salts, especially the sulphate. Retains P_2O_5 in proportion sufficient to form $Al_2(PO_4)_2$. May also contain Fe, Mn, or SiO_2 (hydrated). Possibly also Mg, Zn, Co, Ni, Cu, &c., from which last it may be freed by re-solution and re-precipitation except, perhaps, in the case of Zn, from which a complete separation of $Al_2(OH)_6$ can scarcely be effected. Ca may also accompany it as $CaCO_3$ if the alkaline solution has absorbed CO_2 .

Ign.—Converted to Al_2O_3 . Ignited with NH_4Cl some volatile Al_2Cl_6 may form. After ignition practically insoluble in HCl . Converted to a soluble form by fusion with an alkaline flux.

$Al_2(PO_4)_2$.

Rem.—Of service in the determination of Al in manufactured irons and in mineral phosphates.

Cond.—Fe, if present, should be in the ferrous form. The conditions usually produced are a solution acid with acetic, in which Fe has been reduced by $Na_2S_2O_3$, and containing an excess of alkaline phosphate. This is boiled for some time.

Sol.—Dissolves in mineral acids. Insoluble in moderately strong HCl . Prevented by tartrates, citrates, &c., in the same way as $Al_2(OH)_6$.

Contam.— $Fe_2(PO_4)_3$ and possibly basic ferric salt. If Fe is kept entirely in the ferrous condition (which is not always possible), this contamination would not occur. Remedied by re-dissolving, reducing, and re-precipitating. $Ca_3(PO_4)_2$ (or alkaline salts if the solution is not sufficiently dilute), may also accompany the precipitate. Remedy by re-solution and re-precipitation. Glaser's method for mineral phosphates involves the previous separation of the lime, as $CaSO_4$, by the aid of alcohol (*Zeit. Angew. Chemie*, 1889, p. 636).

$Al_2(OH)_n(C_2H_3O_2)_{6-n}$. Basic Alumina Acetate.

Rem.—Very similar to the corresponding Fe compound. Being more slimy in character, it gives more trouble in filtering and general management. Used for separation only.

Cond.—The same as for the Fe compound. Practically no free acetic acid is admissible. Al should be in the form of acetate. Precipitate obtained by boiling. If boiled too long it filters and washes with more difficulty.

Sol.—Dissolves in acids to some extent in very dilute boiling acetic. If the solution after boiling is allowed to cool, a considerable proportion re-dissolves. Soluble, or precipitation prevented by citrates, tartrates, &c. The small amount almost invariably remaining in the filtrate may be recovered by careful neutralisation and boiling, or better by evaporating to dryness and taking up with dilute acetic.

Contam.—As for the Fe compound. Salts of fixed alkalis, P_2O_5 [in proportion sufficient to form $Al_2(PO_4)_2$] SiO_2 (hydrated), Mn, Zn, &c.

$Cr_2(OH)_6$.

Rem.—In general properties this precipitate resembles $Al_2(OH)_6$, and its management is similar. Its tendency to carry with it other substances requires that it shall

always be re-dissolved and re-precipitated with ammonia at least twice.

Cond.—Absence of members of $(NH_4)_2S$ groups, and preferably of all non-volatile salts. Solution must be exactly neutral (ammonia added in slight excess and then boiled until neutral). NH_4Cl assists the separation.

Sol.—Dissolves in all acids, in fixed alkaline hydrates, and perceptibly in excess of NH_4OH . Soluble or prevented from precipitating by tartrates, citrates, sugar, &c.

Contam.—Salts of fixed alkalis, alkaline earths, members of the $(NH_4)_2S$ group, &c. (See above, *Rem.*)

Ign.—Converted to Cr_2O_3 , in which form, if strongly ignited, it becomes insoluble in HCl . In presence of fixed alkalis or alkaline salts and in contact with the oxygen of the air, is partially or entirely converted to chromate.

(To be continued).

ON THE OCCURRENCE OF NITROGEN IN URANINITE, AND ON THE COMPOSITION OF URANINITE IN GENERAL.*

By W. F. HILLEBRAND.

(Continued from p. 222.)

Methods of Analysis.

ORDINARILY not less than 2 grms. was taken for the main analysis. Solution was effected in the least possible quantity of weak nitric acid at the temperature of the water-bath, so as to dissolve as little of the gangue as possible. When disengagement of gas bubbles had entirely ceased the uranite was decomposed. Any black powder then remaining was treated as gangue, being columbite. The gaseous products of decomposition of the nitric acid are but faintly reddish. After filtering, the insoluble matter was ignited and weighed. A necessary refinement, in cases where the amount of gangue is appreciable, is to weigh it at $100^\circ C.$, and then to ascertain how much, if any, water it contains. The filtrate was evaporated to dryness in platinum to obtain soluble silica, which after weighing was tested as to purity by hydrofluoric and sulphuric acids. From the filtrate lead was thrown down by hydrogen sulphide, and weighed eventually as sulphate. Iron and manganese were then removed as sulphides, while the earths and uranium were held in solution by ammonium carbonate and ammonia. This was effected in a flask of not over 250 c.m.³ capacity, in which the precipitate was allowed to settle over night. A precaution to be observed is to add ammonia as well as ammonium carbonate, otherwise the earths thrown down with uranium on neutralisation of the originally acid solution will be only partially re-dissolved. In order to ascertain this it is best to remove the hydrogen sulphide from the filtrate from lead sulphide before proceeding to the precipitation of iron. On adding ammonia and ammonium carbonate it can then be readily seen when the earths are dissolved, which is not at all easy if the hydrogen sulphide has not been first expelled. Calcium could rarely be found with the iron. The sulphide precipitate and the filter were roasted and weighed as a check, and then iron was separated from manganese if necessary, and the amount of the former determined as Fe_2O_3 , which was generally checked by re-solution, reduction by hydrogen, and titration by potassium permanganate.

If any doubt had existed as to the completeness of separation from the earths, the iron and manganese were a second time precipitated as sulphides in the presence of ammonia and ammonium carbonate.

The filtrate or filtrates, as the case might be, were

* From "Bulletin No. 78, U.S. Geological Survey, 1889-90." An abstract of this paper was published in the *Am. Jour. Sci.*, vol. XL, p. 384.

gently heated till all ammonium carbonate was driven off, the precipitate was dissolved in nitric acid, and separation of earths and uranium from any traces of magnesia and alkalies present effected by freshly prepared ammonium sulphide, allowing to digest for an hour in a covered platinum dish on the water-bath. As others have experienced, it was found that no separation from calcium can be effected by this method. While this element was always present in small quantity, it could very rarely be detected in the filtrate. Nevertheless the above method was preferred to that of Alibegoff (*Ann. d. Chem.*, 1886, vol. ccxxxiii., p. 133), in which uranium is separated from alkaline earths, magnesium, and alkalies by mercuric oxide, because of the necessity of converting the nitrates into chlorides for the success of the latter operation, whereby an additional reagent is employed and the manipulations are increased, both of which it was desired to reduce to a minimum.

From the precipitate of earths and uranous oxide mixed with sulphur, the oxides were extracted by nitric acid, the solution was evaporated to dryness, water was added, and then, when boiling, oxalic acid and two or three drops of ammonium oxalate. The precipitated oxalates were washed in due time with weak oxalic acid solution, ignited, and preserved in the crucible till later. The filtrate, which still always contains some rare earth metals and calcium, was evaporated to dryness, ignited to destroy oxalates, re-dissolved in nitric acid, and evaporated with sulphuric acid in quantity slightly more than sufficient to convert into sulphates. After removal of all nitric acid the residue was dissolved in a little water, and two and a half to three times the bulk of alcohol was added. In the course of twelve hours or more the precipitate, containing all the calcium not originally thrown down by oxalic acid, besides some sulphates of the rare earths, was collected on a filter, washed with alcohol, dried, dissolved in weak nitric acid, and the rare earths were separated from calcium by ammonia and weighed with the main portion.

The alcoholic filtrate was evaporated to dryness, ignited, dissolved in nitric acid, and the precipitate produced by boiling with ammonia was ignited repeatedly in air and in hydrogen until a constant weight was reached by reduction. The UO_2 thus obtained was apparently never entirely free from rare earths, amounting usually to a quarter or a third of a per cent of the mineral. They were in two analyses recovered by treating the perfectly dried nitrates with ether, filtering, washing with ether, dissolving the insoluble nitrates of the earths and some uranium in water acidulated with a drop of nitric acid, and then adding oxalic acid to the hot aqueous solution after evaporating to dryness. The earths were weighed with the already tared main portion, and a proper deduction was made from the uranium oxide. It is best always to make a second precipitation by ether to insure extracting the last traces of earths from the uranium.

The earths as weighed contain the balance of the calcium and a small quantity of uranium. Solution was effected by prolonged digestion with sulphuric acid somewhat diluted, repeated after filtration if necessary. Thorium, cerium, lanthanum, and didymium were then separated from the yttrium earths by potassium sulphate in as nearly neutral a solution as could be obtained. Thorium and cerium were separated from lanthanum and didymium by long passage of chlorine gas through a solution of sodium hydrate holding the gelatinous hydrates of the earths in suspension. Finally, thorium was separated from cerium by boiling with sodium hyposulphite. Small quantities of what might be zirconia were now and then found, but its identity could not be proved.* The turmeric paper test for this element has never proved of any value in my hands where small amounts of it were present. The earths of the yttrium

group and the uranium were precipitated from the potassium sulphate solution by ammonia, re-dissolved in nitric acid, the solution was evaporated to dryness, and the earths were precipitated from aqueous solution by oxalic acid and weighed, after which they were examined for calcium, as was also the filtrate from them containing the uranium and that containing the potassium sulphate, in both of which calcium might be found. The combined calcium oxide was deducted from the original weight of the earths and added to the lime earlier separated by alcohol. The small amount of uranium recovered—usually 4 to 7 m.grms. as UO_2 —was likewise deducted from the earths and added to the main portion.

In the last analysis of Glastonbury uraninite, which was made especially with a view to great accuracy in summation, and in Analysis XVIII., a modification was introduced at one point which is perhaps worthy of retention in future work. Instead of evaporating the filtrate from iron sulphide to complete removal of ammonium carbonate, the gradually forming precipitate of carbonates was removed by filtration at a point where the earth carbonates are almost entirely thrown out and the uranium is still in solution. A little practice enables one to recognise this point readily. When the filtrate is treated as already described in the first method, oxalic acid will generally fail to show any earths present with the uranium, but the precipitation by alcohol, and later by ether, must not be neglected. The carbonates are now dissolved in nitric acid, the solution is evaporated to dryness, and the rare earths are separated by oxalic acid in perfect purity, except perhaps for a little lime, from the small amount of uranium they contain. The resulting filtrate will always contain a little of the earths, for it has been my experience that the precipitation by oxalic acid is never absolute. It is best to unite it with the main portion of uranium and separate lime and some of the earths at the proper stage by alcohol, and from the weighed UO_2 the remainder of the earths by ether. So far as my limited experience with this modification goes it has proved satisfactory and decidedly preferable to the procedure first given, the chief point gained being that a purification of the earths from uranium is unnecessary and the trustworthiness of the weight found for the combined earths is heightened.

It may be said, as regards the purity of the different earths or groups of earths after separation, that, whereas the original ignited mixture was somewhat dark, without sharply characterisable colour tint, the thorium was pure white and gave the theoretical molecular weight; the ceric oxide dissolved with a strong yellow colour in concentrated sulphuric acid, which was bleached instantly by sulphurous acid, and with lead peroxide and nitric acid it gave likewise a deep yellow colour; the lanthanum and didymium were cinnamon-brown in colour, soluble in weak nitric acid, and the gelatinous precipitate by ammonia from acetic solution gave sometimes a blue colour with powdered iodine, due to lanthanum; the yttrium earths were pale straw-coloured, and dissolved very readily in weak acids. Although only a single separation of the yttrium group by potassium sulphate was made, it was probably nearly perfect, for any remainder should have been obtained subsequently with the lanthanum and didymium, and the quantity of these was so small as to preclude much contamination by earths of the yttrium group.

Concerning the estimation of magnesia and alkalies, and traces of phosphoric acid, nothing need be said.

Water was estimated by heating the mineral in a current of air and collecting the water in a calcium chloride tube. In only one case—the last Glastonbury analysis—was the mineral fused in a boat with sodium carbonate in order to retain the substance or substances which imparted to the water expelled by simple ignition an acid reaction. The weight of water found was hereby slightly reduced, and perhaps a similar result would have followed the taking of a like precaution in other cases.

* Except in the Colorado uranite, which contains practically no other earths than zirconia.

The acid property of the water was perhaps due to fluorine, since a trace was found in the Glastonbury mineral, but by no means enough to account for even the slight difference observed between the gains of the absorption tube by the two modes of ignition.

The correct estimation of UO_2 is of the utmost importance, and it was in consequence of remarkable variations in results first obtained that much material, which would have been of inestimable value at a later period, was used up in endeavours to secure concordance. An obvious source of error at first was the formation, in the sealed tubes in which decomposition of the mineral with rather strong sulphuric acid was effected, of bright green crystals of a thorium-uranous sulphate which were almost insoluble in water, and hence necessitated such a length of time for titration as to seriously discredit the results. Dilution of the acid proved a remedy for this difficulty, and perfectly satisfactory solution* was obtained with one volume of concentrated sulphuric acid to six volumes of water. This proportion was employed in all subsequent work by this method, and decomposition of the uraninite was generally complete by leaving the tubes in an air-bath over night at a temperature of 150° to 175°C . The end reaction with potassium permanganate was then always sharp and satisfactory, but the results were still discordant. The cause was eventually found to be in the manner in which the tubes were filled with carbon dioxide. This was done by introducing either solid sodium carbonate or a solution of the same, and sealing as quickly as possible. It is, however, almost impossible to prevent access of air, often in considerable amount, through the drawn-out neck of the tube before the seal can be made. The following figures are the results of titration on one sample of Glastonbury uraninite. They are tolerably concordant compared with other series, and yet are undoubtedly one and all too low. UO_2 found 55.00, 54.12, 56.98, 55.93, 56.15, 55.61. Every now and then a result would fall so far below all others of a series as to be positively startling.

When, however, the tubes were filled with carbonic acid from an external generator through a fine glass tube drawn out of the same kind of glass as that of which the decomposing tube consisted, and the fine tube was sealed into the other while the gas continued to pass, all air except the trace in the carbonic acid itself was excluded, and after decomposition the titration results showed a concordance and accuracy that could not be surpassed, as shown by the following series made on carefully purified U_3O_8 , using freshly boiled distilled water:—

UO_2 found 32.11, 31.90, 32.15, 32.12, 32.06, 32.17, 32.28. Theory requires 32.07.

That it is immaterial whether the water is free from oxygen or has stood for some days exposed to the air is shown by the following series, in which water several days old was used:—

UO_2 found 32.11, 31.85, 32.37, 32.36, 32.13.

An excess over theory is to be expected, for it is difficult to prepare U_3O_8 with the theoretical percentage of UO_2 .

In order to test the probable error of previous titrations the following determinations were made, in which the tube was filled as carefully as possible with carbonic acid by using a solution of sodium carbonate:—

* Although the green crystals were no longer formed, there still appeared, as when stronger acid was used, a curious crystallisation, taking the form of excessively fine needles woven into a felt-like mass which covered the surface of the liquid from end to end of the tube, and when put in motion by a movement of the solution resembled an undulating white rope. This was readily soluble in water, and did not affect the titration at all, but it was observed on a few occasions, when the heating of the tubes was continued for several days, that it gradually disappeared, and in its place an abundant crop of unusually large and clear green crystals was formed. Of the latter, 0.5209 grm. gave on analysis:— UO_2 49.53, ThO_2 3.61, SO_3 32.32, H_2O 13.59; total, 99.05; whence is derived the molecular ratio $\text{UO}_2(\text{ThO}_2)_2\text{SO}_3\cdot\text{H}_2\text{O}$ as 12.06:3.84, and the formula $(\text{UTh})_2\text{O}_4(\text{SO}_3)_2\cdot 4\text{H}_2\text{O}$. Being formed from a much more dilute acid they may possibly differ from the crystals deposited from strong acid in the number of molecules of water. It is intended to make a more thorough examination of this salt at some future time.

UO_2 found 31.06, 31.07, 29.72, 29.33, 29.89, 30.69.

Theory requires 32.07.

Two out of the three experiments by Zimmerman (*Ann. d. Chem.*, 1886, ccxxxii., 287, lines 5 and 6)), in which UO_2 in U_3O_8 was estimated by permanganate after solution by hydrochloric acid in sealed tubes, using manganese sulphate to counteract the effect of the acid, gave 31.39 UO_2 instead of 32.07.

Finally a set of tests was made on a specimen of North Carolina uraninite in order to ascertain the degree of concordance to be reached on the mineral.

UO_2 found 38.14, 38.12, 38.12, 38.04, 38.07, 37.97, 37.87. Solution in the last two cases had been effected at 100°C ., and was, perhaps, not quite perfect.

It is thus apparent that, with due regard to the exclusion of all air from the tube, the method leaves nothing to be desired as regards accuracy. The acid employed was specially distilled, and gave with brucine and diphenylamine no indication of nitric acid, the test being made as prescribed by Wagner (*Zeit. f. Anal. Chem.*, 1881, p. 329 ff.), and it was absolutely without decolorising power on permanganate. When wanted, a portion was diluted with about 12 volumes of water, and boiled down to half the bulk, when it was rapidly cooled. In the meantime the mineral, in quantity from 0.3 to 0.5 grm., having been introduced into the tube, about 2 c.m.³ of distilled water was added, and brought to boiling for a few moments in order to expel air from the powder. When somewhat cooled, from 15 to 30 c.m.³ of the dilute sulphuric acid, according to the amount of mineral and the size of the tube, was added, and then the carbonic acid, which had been allowed to generate and escape from the apparatus for some time, was introduced, and the seal was made as above described. No breakage of a tube in the oven ever occurred as a consequence of fusing the one tube into the other. The titrations were made in about half a litre of water, to which sulphuric acid had been added, as rapidly as possible, using a dilute solution of potassium permanganate, giving about 0.00036 grm. oxygen to the cubic centimetre that had been standardised by iron wire of known contents in iron and checked by pure oxalic acid, and taking account of the expansion or contraction of the titre liquid if its temperature varied more than a few degrees from that possessed by it at the time of standardisation.

Zimmerman (*Ann. d. Chem.*, 1886, ccxxxii., 285) decomposed U_3O_8 for the purpose of estimating UO_2 by concentrated sulphuric acid in a current of carbonic acid, but this method is not very applicable to uraninite, owing chiefly to its greater insolubility, particularly when rich in UO_2 . Whereas, according to Zimmerman, quantities of U_3O_8 up to 1.2 grms. are decomposed thus in an hour, uraninite may be only moderately attacked after many hours boiling. The whitish green insoluble salt which soon separates out undoubtedly exerts a retarding effect in protecting the rest of the uraninite powder from the action of the acid. A couple of tests were made by this method which accorded fairly well with the others, but owing to the great uncertainty of securing complete decomposition they were not multiplied.

In the early part of the present investigation, when want of concordance in the results of UO_2 titrations was the rule, decomposition by hydrofluoric acid was sometimes employed as a method leading to the estimation of UO_2 gravimetrically, and the results go to show that this may be developed into a method of considerable accuracy, useful at any rate as a check upon the volumetric determination.

All uraninites, without exception, are decomposed completely by hydrofluoric acid, even in the cold, if time enough is given, the uranous uranium being thrown down with the earth metals and lead as an insoluble fluoride. The refractory Glastonbury variety was thus decomposed in about ten days. In order to accelerate action, the acid and very fine powder were placed in a wide and perfectly flat platinum dish provided with a loose fitting

cover, which was set in a dentist's vulcaniser containing a solution of sodium carbonate to absorb acid vapours. Dish and vulcaniser having been filled with carbonic acid gas, the lid was adjusted and a lamp placed beneath, so that decomposition should take place under high temperature and pressure, and in absence of air. The main difficulty in the subsequent manipulation, and probably the only element involving possible serious error, is the difficulty of washing the precipitate on the filter, owing to its strong tendency to run through as soon as washing begins. Experience seemed to show that this is best obviated by using water containing ammonium chloride and hydrofluoric acid, but the experiments made were too few in number to show whether the method can be developed into an exact quantitative one. An attempt will perhaps be made to perfect it. The following are some of the results obtained:—

A specimen of Glastonbury uraninite, giving on a basis of 57.43 per cent UO_2 by titration 26.48 per cent of UO_3 , gave gravimetrically 26.89 and 28.58 per cent UO_3 .

Another specimen from Glastonbury, giving by titration 59.31 per cent UO_2 , gave gravimetrically 60.05 per cent.

Colorado uraninite, giving 58.51 UO_2 by titration, gave 58.24 per cent gravimetrically.

A few trials with U_3O_8 gave results in part less satisfactory, namely, 34.89, 31.26, and 28.47 per cent UO_2 instead of 32.07.

Assuming the practical insolubility of UF_4 in hydrofluoric acid, the method should give a tolerably exact separation of UO_2 from FeO and UO_3 , and thus in connection with the oxygen used in titration indicate the state of oxidation of iron, as well as uranium, in substances containing both where one does not predominate so enormously over the other as in uraninite. Even from Fe_2O_3 the separation should be exact, unless in the moment of breaking up of the molecule the ferric iron should exert an oxidising effect on the uranous uranium before the latter is withdrawn from its influence by combination with fluorine. Hydrogen sulphide being without reducing effect on UO_3 , the presence of sulphides would be immaterial so far as the separation of UO_2 from UO_3 and the oxides of iron is concerned, but of course the correct estimation of total oxygen by titration would be impossible if iron were present in its peroxidised state, or if even in its absence the hydrogen sulphide formed could not be expelled before titration.

It may be worth while before leaving the subject of estimation of uranium to add that, in accordance with Zimmerman's observations, I have met with no evidence of the existence of an oxide U_2O_3 as a result of strong heating in air; and the oxide U_3O_8 , as he has so conclusively shown, is also, by my own experience, only to be obtained with its theoretical percentage of oxygen by igniting and cooling in oxygen.

(To be continued.)

Detection of the Contamination of Water with Sewage.—Peter Griess (*Ber. Deutsch. Chem. Gesell.*).—The author dilutes paradiazobenzol sulphuric acid with 100 parts of water, and adds a little soda-lye in excess. The solution must always be used when fresh, as it soon becomes coloured spontaneously. The water to be examined is placed in a tall cylinder of colourless glass holding about 100 c.c., which is placed before a window upon a white surface. To the water are then added 2 to 4 drops of the diazo-solution. The whole is well stirred up and it is carefully observed. If no change of colour takes place within five minutes we may infer the almost entire absence of organic excretions or products of decomposition. A yellow colour more or less decided shows the presence of a more or less considerable quantity of such matter. By means of this reaction the author has detected normal human urine when diluted with 5000 parts of water, and the urine of horses when diluted with 50,000 parts.

THE MANCHESTER SHIP CANAL FROM A SANITARY POINT OF VIEW.

PUBLIC attention is being authoritatively called to a serious peril to which this project—otherwise highly commendable—is exposing the towns on its banks and the districts which it intersects. Everyone knows that the population of South Lancashire is inferior in numbers to that of London alone; that the quantity of industrial refuse to be got rid of is much larger, and that the volume of water carried by the Irwell and its affluents is very much smaller than that of the Thames. Hence it is justly contended that if all this pollution is allowed to collect in the new canal, and there to remain without regular removal by a powerful current, a nuisance will be created which it is simply fearful to contemplate. The directors of the Canal Company and their advisers, though without the gift of prophecy, might have been expected to foresee and provide against such a peril. All Lancashire men know what the river Irwell and the Bridgewater Canal have been for more than half a century. Pour the two together and the consequence must be a Stygian pool such as the world has not yet witnessed. It therefore behoves the Canal Company to be wise in time. They are being warned that unless this prospective danger is guarded against, Parliament may put its veto upon the completion of an undertaking which already presents an aspect so menacing. Surely the shareholders will consider that even the extra outlay which will be required for the sanitation of the undertaking will be a less blow to their interests than its total arrest. It will be necessary to purify the sewage and other waste waters of Manchester and Salford before allowing them to enter the canal.

This can be effected only by precipitation. The large quantity of chemicals present will be a total bar to irrigation. The foul water cannot, fortunately, be carried out to sea by any modification of the Bazalgette system. Nor can the country afford to take any more steps in the costly and wasteful way of precipitating the sewage (imperfectly) and conveying the deposit out to sea. As the *Liverpool Journal of Commerce* appropriately remarks—"Any system of sewage disposal which entails the waste of the offensive matter is essentially wrong and opposed to all principles of science and common sense."

It adds further that "no system of sewage disposal can fulfil the essential conditions unless adequate chemical precipitation is provided for, and at the same time means are adopted for the disposal of the precipitated matter as manure."

These are the very principles which we have long maintained, and we are glad to find that they are being adopted by the general press. Of course, we in London have little room to take up our parable against Lancashire as regards the neglect or rather the toleration of nuisances. The London County Council seems, unfortunately, to have inherited the errors of its predecessor, the Metropolitan Board of Works. Perhaps, indeed, such questions as Public Health are overlooked by Boards because they do not fall in with the demands of fashion.

Adulteration of Rape-Oil with Fish-Oil.—O. Schweissinger (*Pharm. Central Halle*).—The following characteristics may serve for the detection of the latter oil:—

	Rape-Oil.	Fish-Oil.
Specific gravity at 15°	0.915	0.931
Saponification number	181	218
Iodine number	98	142
Melting-point of fatty acids ..	21	26
Congeeing-point of fatty acids ..	16	19

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, November 2, 1891.

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Institution:—George Frederick Deacon, M.Inst.C.E.; Miss Henriette Hertz; Arthur Walter Mills; Robert Mond, B.A., F.R.S.E.; Joseph Shaw; D. Hack Tuke, M.D., F.R.C.P.; Lieut.-Col. H. S. S. Watkin, C.B., R.A.; and William Henry White, C.B., F.R.S., M.Inst.C.E.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

UNIVERSITY OF SYDNEY.

A MEETING of the Senate of the University was held on Monday, September 21, 1891, at the University Chambers, Phillip Street.

A letter was received from Mr. F. B. Guthrie, resigning his office of Demonstrator in Chemistry, from January 1 next, in consequence of his appointment as Analyst to the Department of Agriculture. His resignation was accepted with regret.

It was resolved that Professor Thorpe and Professor Ramsay, of University College, London, be requested to select and appoint a Demonstrator of Chemistry to take office on March 1 next, the salary to be at the rate of £350 per annum, and £60 to be allowed for passage money, such sum to be refunded if the demonstrator should resign his office before the expiration of two years from his appointment.

FRANKLIN INSTITUTE.

(CHEMICAL SECTION).

Tuesday, September 15, 1891.

DR. W. H. WAHL, President, in the Chair.

A PAPER by MR. CABELL WHITEHEAD, of the Mint Bureau, in Washington, on "*The Use of Cadmium in Assaying Gold Bullion*," was read by the Secretary in the absence of the author. Dr. Tuttle commented upon the paper, and discussed the most important advantages of the proposed method.

MR. WALDRON SHAPLEIGH, of the Welsbach Incandescent Gas Light Company, of Gloucester, N.J., exhibited the following specimens of *Salts of the Rare Earths*:—

Praseodymium, neodymium, and lanthanum oxides, sulphates, nitrates, chlorides, carbonates, oxalates, acetates, and double salts with the alkaline metals.

Cerium oxide, oxalate, chloride, nitrate, and the double nitrate of the cerous and ceric oxides with ammonium.

Yttrium and erbium nitrates, oxides, and oxalates.

Zirconium oxide, nitrate, sulphate, and some double salts.

Yttrium and erbium (not separated) oxides and nitrates obtained from gadolinite, cerite, monasite, fergusonite, and samarskite. Thorium and vanadium salts.

Also large specimens of the following minerals from which these salts were obtained:—Samarskite, zircon crystals, and monazite sand from North Carolina, monazite sand from Brazil, gadolinite from Texas, and allanite from Virginia.

MR. SHAPLEIGH said the collection was of interest, as it is the first time the salts of praseodymium and neodymium have been shown, and probably separated in this country. Some of the salts have not been heretofore prepared.

The separation of these elements is long and tedious; the specimens shown have undergone nearly 400 fractional crystallisations, and have been in state of constant preparation since early in 1888. Tons of cerite and monazite sand have been used, and tons of the salts of cerium and lanthanum obtained, but the yield of praseodymium oxide has been only a few kilos. The percentage of neodymium is much higher.

Dr. Carl Auer von Welsbach, in 1885, was the first to separate didymium into these elements, and together with Prof. Bunsen, to determine their atomic weights; that of Pr 143.6, and of Nd 140.8. The oxides are M_2O_3 , and probably M_4O_7 .

With one exception, the salts of praseodymium exhibited were of a pale green, and of neodymium pink or amethystine colour.

Zirconium, lanthanum, and cerium should no longer be classed among rare earths, as hundreds of tons of ores from which they are obtained have been located in North Carolina, and there seems no end to the deposits of monazite sand—one of the richest ores, and containing most of the rare earths. In Brazil it does not have to be mined, as it is in the form of river sand. In North Carolina it is found in washing for gold.

Should the arts, trades, or manufactures create a demand for these so-called rare earths, nature could readily supply it from these two localities.

Thorium and yttrium minerals are not so easy to obtain; they have, however, recently been found in quantity in North Carolina and Texas.

Working on a commercial scale, he finds the yield of lanthanum from cerite nearly 1 per cent higher than stated in the analysis published.

NOTICES OF BOOKS.

Foundations of Chemistry. (Grundlagen der Chemie).

By D. MENDELEEFF, Professor at the University of St. Petersburg. Part 7. St. Petersburg: Ricker, 8vo., pp. 143.

THIS part of Prof. Mendeleeff's great work treats of the elements sulphur, selenium, tellurium, chromium, molybdenum, tungsten, uranium, and manganese, and begins the consideration of iron. The author considers that the interior of the earth is a mass consisting like meteorites of siliceous matter and metallic iron mixed with carbides, whilst the lighter bodies, *i.e.*, those with lower atomic and molecular weights, have collected on the surface of the globe. He points out that velocity in mechanics and velocity in chemistry have nothing in common save the idea of time.

Prof. Mendeleeff protests that Berthelot's compound S_2O_7 cannot be regarded as a persulphuric acid, since it forms no salts, and is liable to spontaneous decomposition with absorption of heat. It is properly a sulphur peroxide analogous to hydrogen, sodium, and barium peroxides.

CORRESPONDENCE.

ALLOTROPIC SILVER.

To the Editor of the Chemical News.

SIR,—IN a recently published lecture, Mr. Meldola seems to call in question the existence of allotropic silver. This opinion does not appear, however, to be based on any adequate study of the subject, but to be somewhat conjectural in its nature. No experimental support of any sort is given, and the only argument offered (if such it can be called) is that this altered form of silver is analogous to that of metals whose properties have been greatly

changed by being alloyed with small quantities of other metals. Does, then, Mr. Meldola suppose that a silver alloy can be formed by precipitating silver in the presence of another metal from an aqueous solution, or that one can argue from alloys, which are solutions, to molecular compounds or lakes? Moreover, he has overlooked the fact that allotropic silver can be obtained in the absence of any metal with which silver is capable of combining, as in the case of its formation by the action of soda and dextrine. Silver cannot be alloyed with sodium.

Mr. Meldola cites Prange as having shown that allotropic silver obtained with the aid of ferrous citrate contains traces of iron, a fact which was published by me several years earlier, with an analytical determination of the amount of iron found. Mr. Prange repeated and confirmed this fact of the presence of iron (in this particular case), and my other observations generally, and was fully convinced of the existence of both soluble and insoluble allotropic silver. Mr. Meldola's quotation of Mr. Prange would not convey this impression to the reader.

Of the many forms of allotropic silver, two of the best marked are the blue and the yellow.

Blue allotropic silver is formed in many reactions with the aid of many wholly different reagents. To suppose that each of these many substances is capable of uniting in minute quantity with silver to produce in all cases an identical result the same product with identical colour and properties, would be an absurdity.

Gold-coloured allotropic silver in thin films is converted by the slightest pressure to normal silver. A glass rod drawn over it with a gentle pressure leaves a grey line behind it of ordinary silver. If the film is then plunged into solution of potassium ferricyanide it becomes red or blue, whilst the lines traced show by their different reaction that they consist of ordinary silver. Heat, electricity, and contact with strong acids produce a similar change to ordinary grey silver.

These reactions afford the clearest proof that the silver is in an allotropic form. To account for them on suppositions like Mr. Meldola's would involve an exceedingly forced interpretation, such as no one who carefully repeated my work could possibly entertain.—I am, &c.,

M. CAREY LEA.

Philadelphia, October 22, 1891.

THE CONSTITUTION OF BUTTER.

To the Editor of the Chemical News.

SIR,—On the 19th of January, at the invitation of the Society of Chemical Industry, I read a paper on Butter, and described an experiment on 50 grms. of butter-fat. From that experiment, which I carried out myself, and for the substantial accuracy of which I am able to vouch, I drew some important conclusions which I expect will be verified by competent observers in due course.

The experiment and the conclusions were, as I expected, distasteful to a certain section of my auditory, which was violently demonstrative in its disapproval, but, as I thought, very ineffective in its attempts at criticism. My reply, as recorded in the Society's Journal, winds up with the assertion that I had no doubt of the accuracy of the work that I had brought before the meeting.

Among my auditory was Mr. Allen, of Sheffield, who took part in the discussion, and then some months afterwards, with that fresh in his recollection, presented himself to the Chemical Section of the British Association at Cardiff, and informed the Chemical Section that Messrs. Wanklyn and Fox had never published such an experiment. Having been taken to task, Mr. Allen replies that his statement was perfectly correct as it stands, but seems to be unconscious that his statement to the Chemical Section was calculated to mislead, and no doubt did mislead, the Section.—I am, &c.,

J. ALFRED WANKLYN.

REACTIONS OF ANTIMONY AND ARSENIC.

To the Editor of the Chemical News.

SIR,—Experimenting for some time past upon the action of H_2SO_4 on the gases AsH_3 and SbH_3 , I find that when either of these gases is bubbled through H_2SO_4 , at 160° to 180° C., a partial decomposition of the gas takes place, with formation of a metallic mirror and a solution of the metal in the H_2SO_4 (which can be precipitated as sulphide upon cooling and adding H_2S), whilst a portion of the original gas passes over.

Obtaining a number of mirrors, "Marsh's test," I exposed them to the hot vapours of H_2SO_4 for (say) five minutes, and found that, whilst H_2S was without action upon them, a drop of $(\text{NH}_4)_2\text{S}$ yielded a distinct sulphide, Sb_2S_3 forming almost immediately and As_2S_3 after some time.

I next led $\text{AsH}_3 + \text{H}_2\text{S}$ through a little H_2SO_4 kept just at the boiling-point, and found that As_2S_3 was formed inside of the leading tube, just about where it dips into the H_2SO_4 and also formation of SO_2 . The acid dissolves the sulphide, and it is better to continue the boiling for some time (not strong) to make sure that it is all dissolved, as a precipitate of S forms in the upper part of the tube, which might be misleading; besides, the SO_2 must be boiled off to obtain the dissolved sulphide by the addition of H_2S after cooling. $\text{SbH}_3 + \text{H}_2\text{S}$ behaves in a similar manner.

In the event of excess of AsH_3 or SbH_3 a metallic mirror will be formed. The re-precipitated sulphides, by the addition of H_2S , are fainter in colour than in an HCl solution.

This naturally suggested treating the combined gases as in "Marsh's test," and the experiment resulted in a beautiful coloured sulphide.

Here, also, excess of the metal tends towards the formation of a metallic mirror. The tube must not be strongly heated, else the newly formed sulphide is decomposed and a glazed orange-coloured residue of sulphur is left. Arsenic gives a fine yellow merging to orange and sometimes to ruby-coloured sulphide, which is nearly all deposited on the off-side of the flame. Sb gives a fine ruby-coloured sulphide having an orange edging, and is deposited upon both sides of the flame.

Both sulphides are soluble in NaHO , and are re-precipitated by acidifying with HCl.

I next lighted a small jet and let the flame be as small as possible, and pressed a cold porcelain surface on the flame. Sb yielded a pronounced orange-red sulphide, As a fine canary-yellow. H_2S , under the same conditions, yields a precipitate of pale yellow S, but the two are easily distinguished from one another.

As_2S_3 having the appearance of being dropped on, S has a glazed appearance. As_2S_3 is soluble in a drop of NaHO , S is not, and, when a drop of AgNO_3 is placed upon each, the As_2S_3 begins at once to change to brown and finally to black, whilst S is not affected. These last two reactions will be found very definite in colour and sensitive to the presence of As or Sb, besides having the advantage of dispensing with all intermediate reactions lying between the formations of the gas and sulphide.

With regard to details, use an ordinary $\frac{1}{2}$ test-tube for the generating of the gas, as it yields far better results than when a flask is made use of. Connect the generating tube to a three-limbed tube, do the same with H_2S flask, then to the third limb connect the tube holding the H_2SO_4 , having a small leading tube reaching to the bottom of the acid. In starting let the hydrogen come away freely before passing in the H_2S , as, were it to come away first, it would pass over into the other tube and form a sulphide of the metal when its solution is put into the generating tube, and this holds good during the experiment if the H_2S be too strong.

When testing by the dry reaction it is better to heat at two or three points, as at the lower temperature

required more of the combined gases pass over than one flame can decompose, the presence of which can be detected by lighting a small jet of the gas. — I am, &c.,

MATTHEW FORBES.

12, Bell Street, Dundee.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 16, October 19, 1891.

The Allotropic Conditions of Silver.—M. Berthelot.—The author called the attention of the Academy to the memoirs of Carey Lea on the allotropic states of silver, and exhibited specimens of the colour of gold and others of a purple colour sent him by the author. He explained the importance of these results, which remind us of the work of the ancient alchemists, but he reserved the question whether these substances are really isomeric states of silver or complex and condensed compounds, sharing the properties of the element which constituted the principal mass (97—98 per cent); conformably to the facts known in the history of the various carbons, of the derivatives of red phosphorus, and especially of the varieties of iron and steel. Between these condensed compounds and the pure elements the continuous transition of the physical and chemical properties is often effected by insensible degrees, by a mixture of definite compounds.

Calculation of the Magnetic Rotation of the Plane of Polarisation of Light.—G. Hinrichs.—A mathematical paper not susceptible of useful abstraction.

A New Process for Determining Nitric Nitrogen and Total Nitrogen.—E. Boyer.—This process is founded upon the reduction of nitric nitrogen into ammonia by oxalates and sulphur in presence of soda-lime. It is deduced from the two following experiments: If we heat to redness in a combustion tube a mixture in known proportions of neutral calcium oxalate, of sodium nitrate, and of soda-lime (0.5 grm. sodium nitrate, 5 grms. of calcium oxalate, and 15 grms. soda-lime), about two-thirds of the nitric nitrogen are reduced to the state of ammonia. This number is a maximum, and it does not vary appreciably if we increase the proportions of soda-lime and calcium oxalate to a given weight of nitrate. But if we cause simultaneously calcium oxalate and sulphur to act upon sodium nitrate in presence of soda-lime (0.5 sodium nitrate, 5 grms. neutral calcium oxalate, 15 grms. soda-lime, 2 grms. sulphur), the reduction of the nitric nitrogen to ammonia is complete. This second reaction the author has applied at first to the determination of nitric nitrogen in potassium and sodium nitrates, then to the determination of the total nitrogen in all its three states (organic, ammoniacal, and nitric) operating as follows: He first prepares a powdered mixture consisting of sulphur 1 part, calcium oxalate 2 parts, soda-lime 6 parts. In the preservation of this mixture no precautions are required save those used for soda-lime. For the analysis he weighs out 0.5 grm. potassium or sodium nitrate dried and powdered, which are intimately incorporated with 50 grms. of the mixture above described. Then into a combustion tube, 0.55 metre in length and 0.017 metre in diameter, he introduces successively, beginning with the closed end, 2 grms. calcium oxalate, for the production of the inert gas required to sweep out the apparatus at the end of the operation, 10 grms. soda-lime in powder, 10 grms. of the mixture, the nitrate to be analysed, mixed as aforesaid, 10 more grms. of the mixture, 10 grms. soda-lime in powder, and finally a plug of asbestos. The

analysis is conducted exactly in the same manner as the determination of nitrogen with soda-lime. The combustion is completed in 40 minutes. The gaseous ammonia is collected in a Will-Varrentrap's tube containing an excess of sulphuric acid of known strength. The determination of the neutralised acid is effected in the ordinary manner, care having been taken to expel by ebullition any sulphuretted hydrogen and carbonic acid which may have been formed during the combustion. The quantity of a nitrate taken for analysis is 50 grms. of the mixture should not exceed 0.5 grm. sodium or potassium nitrate. 1 grm. must be taken of any substance containing nitrogen in all its three states.

The Action of Nitric Acid upon Dimethylated Ortho-Anisidine.—P. van Romburgh.—The product is a dinitro-nitrosamine of monomethylated ortho-anisidine.

Zeitschrift für Analytische Chemie.
Vol. xxx., Part 3.

Determination of Nitrogen.—O. Foerster had continued his researches on the determination of nitric nitrogen (see *Zeitschrift*, xxviii., 422). He has executed comparative determinations of saltpetre, using for the conversion of the nitric acid into ammonia phenolsulphuric acid either alone or along with zinc powder or sodium thiosulphate. The first method did not give satisfactory results. The author obtained values which agreed well with the true quantity of saltpetre on using zinc-powder as a reducing agent according to Jodlbaur's suggestion, omitting the addition of platinum chloride, and using sulphuric acid containing 5—6 per cent of phenol, which, after the saltpetre has been dissolved, is to be mixed with an equal quantity of pure sulphuric acid. He points out, however, that the zinc-powder must be added in very small portions and with refrigeration, and that a large excess of soda-lye must be used to dissolve the precipitate of zinc hydroxide. The experiments with sodium thiosulphate gave quite satisfactory results. He uses by preference a quantity of material containing 0.5 grm. of saltpetre, saturates it with water in the solution flask, distributes the solution of the saltpetre upon the sides of the flask by shaking, and evaporates down in the water-bath. There are then added 15 c.c. of a concentrated sulphuric acid containing 6 per cent of phenol, and the saltpetre is caused to dissolve in the sulphuric acid by frequently moving the flask. As this dissolving takes up some time Foerster considers that Stutzer's agitating apparatus would be useful. The saltpetre dissolves more easily in the water when it has been diffused over the surface of the flask, as above directed by previous solution in water and subsequent desiccation. If the saltpetre is used in the form of powder its solution in the phenol sulphuric acid is more difficult, and the operation must be conducted with the aid of refrigeration. After the saltpetre is perfectly dissolved from 3—5 grms. of crystalline sodium thiosulphate are added, and the acid mixture after the completion of the reaction is diluted with pure sulphuric acid, 0.5 grm. mercury having been added. To 30 c.c. of the phenol sulphuric acid there are used 20 c.c. of the pure sulphuric acid. This dilution is necessary to effect the complete oxidation of the phenol and the other organic substances. The process is then completed according to Kjeldahl's directions. Foerster regards the addition of phosphoric anhydride to the sulphuric acid as also the treatment with permanganate after the sample is dissolved. The author gives various reasons why his process is preferable to Jodlbaur's original method with zinc-powder. The presence of chlorides occasions a small loss of nitrogen, which may be avoided if, when evaporating the solution of saltpetre, the chlorine is precipitated by the necessary quantity of silver sulphate. The silver chloride formed is not in any manner injurious. For the determination of total nitrogen in presence of much organic matter,

nitrogenous and non-nitrogenous, along with nitrates the above described, according to Foerster's experiments, may be used with satisfactory results. A larger addition of pure sulphuric acid is here to be recommended, about twice as much as in the case of pure saltpetre. In many cases it is preferable to omit the previous moistening of the sample and the subsequent drying in the solution flask. On account of the strong frothing on the addition of the phenolsulphuric acid, a solution flask is selected holding 300—400 c.c., and refrigeration is applied whilst the substance is mixed with the phenolsulphuric acid.

With reference to the statements of Scovell and the Association of Official Agricultural Chemists, who recommend the use of salicylic acid in place of phenol in the Jodlbaur process, Foerster has examined whether the determination of nitric nitrogen can be effected with salicylic acid containing sulphuric acid and sodium thiosulphate. He considers salicylic acid decidedly preferable to phenol both in the analysis of pure nitrates and in the determination of total nitrogen in mixtures of nitrates with nitrogenous organic matter. To 0.5 potash salt-petre there are used 16 c.c. of sulphuric acid containing 6 per cent of salicylic acid, 5 grms. sodium thiosulphate, and 10 c.c. pure sulphuric acid. The presence of chlorides occasions in this case, within certain limits, no loss of nitrogen, so that there is no necessity for the addition of silver sulphate. Foerster has obtained perfectly accurate results in presence of about 5 per cent sodium chloride. For further experiments on this subject we must refer to the *Chemiker Zeitung*, vols. xiv. and xv.

For the determination of nitric acid in manures T. F. Schmitt (*Chemiker Zeitung*, xiv., 1410) effects the conversion of the nitric acid into ammonia by means of nascent hydrogen. He proceeds as follows:—40 c.c. glacial acetic acid and 15 grms. of a metallic mixture of equal parts of zinc powder and iron powder are put in an Erlenmeyer flask holding about 750 c.c., 50 c.c. of the solution of nitrate representing 0.5 gm. of the substance are allowed to flow in with constant agitation. The development of hydrogen begins at once and continues for about 15 minutes; after this time 15 grms. more of the metallic mixture are added. The mass often congeals to a paste, but an addition of 30 c.c. of water causes the development of hydrogen to re-commence. In 30—40 minutes the reduction is complete; 200 c.c. of soda-lye, of sp. gr. 1.25, are added, and the ammonia is distilled off in the ordinary manner. Determinations with pure nitrates gave results which agree with the theoretical quantities. The temperature must not be allowed to rise to near 89°; the glacial acetic acid must be present in sufficient excess to combine immediately with all the ammonia; and the soda-lye added after the completion of the reduction must suffice not merely to neutralise the residual excess of acetic acid, but to keep the dissolved zinc hydroxide in solution. The author concludes from his experiments that this method may be used as a substitute for the Jodlbaur process in the determination of total nitrogen in organic matter mixed with nitrates, by first reducing and then heating with concentrated sulphuric acid. A. F. Holleman (*Chemiker Zeitung*) has not found this process quite satisfactory. F. Scheiding (*Chemiker Zeitung*) writes concerning the Schulze-Tiemann method of determining nitric nitrogen. He also proposes an apparatus for collecting and measuring nitrogen when the method of Dumas is used.

Comparison of the Congealing-Points of Different Tallows.—Finkener.—This paper requires the accompanying figure.

Volumetric Determination of the Acidity of Oils.—Holde.—In case of pale oils in the ethereal solution, of which the colour reaction of phenolphthalein may still be observed, 10 c.c. of the sample are measured out, the measuring vessel is rinsed out with a mixture of 8 parts ether and 2 parts absolute alcohol containing phenolphthalein and neutralised, and the liquid after the

addition of the rinsings is titrated with alcoholic soda, 1 c.c. of which is equivalent to 0.005 gm. SO_2 , until a permanent red colour appears. In case of dark oils 20 c.c. of oil and 50 c.c. of absolute alcohol are well shaken up in a cylinder. After the two strata have become separated 25 c.c. of the alcoholic stratum are mixed with alcohol and ether containing phenolphthalein and titrated as above.

Sophistication of Bergamot Oil.—Schimmel and Co. point out that the specific gravity of the genuine oil must not be below 0.880; its optical rotation not more than +20° (for a column of liquid of 100 m.m.). The oil must form a clear solution in $\frac{1}{4}$ part of alcohol at 90 per cent by volume, and the solution must not become turbid on the addition of alcohol of the same strength. The residue should form a green homogeneous mass.

Detection of Ground Wood in Paper.—W. Herzberg.—The well known detection of ground wood-stuff by the red colouration obtained with phloroglucine and hydrochloric acid is not always decisive, as metanil yellow, which is much used in paper making, is coloured red by acids. There is, however, a difference in the appearance of the colour. If phloroglucine is placed upon paper containing ground wood there is very gradually formed a red colour which increases in depth, whilst the thicker fibres are conspicuous by their darker colour. The spot fades away gradually without being surrounded by a halo. In presence of metanil yellow the spot appears at once in its entire depth of colour; it fades in a few minutes and is surrounded by a violet halo. In case of the presence of hemp, unbleached jute, fibres of Adanson, &c., certainty cannot be attained with a microscopic examination.

Examination of Opium and its Alkaloids.—A note by Euge Dieterich (*Pharm. Central Halle*), and P. C. Plugge (*Archiv. der Pharmacie*).

Determination of Urea.—Papers by Mörner and Sjöqvist (*Skand. Archiv. fur Physiologie*), E. H. Bartley (*Journal of the American Chemical Society*), and C. J. H. Warden (*CHEMICAL NEWS*).

Detection and Determination of Hydrochloric Acid in the Gastric Juice.—Notices by Salkowski and Kumagawa (*Archiv. fur Pathologie Anat.*), Sansoni and Molinari (*Annali de Chimica*), Moritz (*Archiv. fur Klin. Medicine*), Favizky (*Archiv. fur Pathologie Anat.*), Bourget (*Archiv. de Med. Exper.*), F. A. Hoffmann (*Central Blatt. fur Klin. Medicine*), and A. Jolles (*Monatshefte fur Chemie*).

Atomic Weight of Bismuth.—R. Schneider (*Journ. Prakt. Chemie*).—The author objects to the results of A. Classen, and considers the value 208 more probable than that given by Classen. Classen (*Journ. Prakt. Chemie*) replies that Schneider's contention is not based upon experimental evidence.

Atomic Weight of Magnesium.—W. M. Burton and L. D. Vorce.—(From the *CHEMICAL NEWS*).

The Equivalent Weight of Fluorine.—Henri Moissan.—(From the *Comptes Rendus*).

Journal of Inorganic Chemistry.—A journal embracing the entire field of inorganic chemistry is about to be issued by Leopold Voss, 18, Hohe Bleichen, Hamburg. The editor will be Prof. Dr. Gerhard Krüss, of Munich (Herzog Heinrich-strasse 4). The new paper will be devoted to inorganic researches and to theoretical treatises belonging to this sphere. Analytical methods of a purely scientific character are admissible, but those which relate to technical chemistry are excluded. It will be admitted that for a quarter of a century inorganic chemistry has ceased to be a merely descriptive discipline, and has begun to participate in the decision of theoretical questions. A number of the most eminent cultivators of inorganic chemistry will co-operate in the new undertaking.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Laboratory without Gas.—In reply to "F.I.C.'s" query, I beg to inform him that I have worked a tolerably large laboratory for nine years in a gas-less district with the following appliances. For heating, boiling, distilling, &c., I use a Ripplingill's "Hero" stove, which burns petroleum. If the top of this stove be covered with wire gauze it will be found a most satisfactory substitute for the ordinary Bunsen. For larger distillations, &c., at higher temperatures, I use a "Duplex Hero," which is also convenient for heating a small drying oven or water-bath. The "Giant Hero" will heat a large drying oven or a number of heaters, &c. I can recommend these stoves highly for simplicity, efficiency, and non-liability to get out of order. For low heats I use either the common or the Argand spirit-lamp, and the Russian blast spirit-lamp for small fusions. For very high temperatures Fletcher's gasoline blowpipe answers every purpose and is also adaptable to this maker's excellent portable furnaces for metallurgical work. With such an outfit "F.I.C." should never feel the want of gas. I shall be glad to supply any further information as to details which he may require.—BRYAN CHARLES WALLER, M.D., F.I.C.

Laboratory without Gas.—In answer to the query of "F.I.C." I desire to say that I was chemist at a large iron works in England in the laboratory of which there was no gas. The principal heating arrangement in use was a large sand-bath heated by means of a coal fire. It was not unlike a baker's oven, only more open, and in place of the stone floor there was a layer of 3 or 4 inches of fine sand, the heat being regulated by a damper. Being always accustomed to the use of gas heaters I took very badly to this arrangement at first, but after getting into the way of using it I greatly preferred its use to that of gas Bunsens or Argands. In a properly built furnace the heat can be regulated by the damper to a nicety, and the furnace is so arranged in relation to the sand-bed that the heat gradually increases from the front (or outside edge) to the back. A constant supply of distilled water can also be had by making use of the heat from this fire.—D. J. P.

TO CORRESPONDENTS.

H. E. H.—Persons evidently means by "A B" Baumé's areometer. There is no certainty which of the existing scales of that instrument he used. It can scarcely have been the American.

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THE CHEMICAL NEWS.

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DETERMINATION OF THALLIUM.

By M. H. BAUBIGNY.

In the earlier researches made upon thallium the sparing solubility of thallous iodide in water suggested this compound as a means of determining this metal. In fact, experiment has proved that the iodide is almost the only salt utilisable for this purpose. It is less soluble than the bromide and the chloride, and stable even above 100°, whilst the peroxide and the sulphide—the most insoluble compounds—are affected by desiccation. Still the insolubility of the iodide in water is not sufficient for the degree of accuracy required in analysis. It is only when the liquid contains certain salts, and especially potassium iodide, as observed by Lamy, Willm, and Werther, that the solubility of thallous iodide is considerably less and becomes null.

Willm, who has practised this method of determining thallium, says that it is far from being exact, since a fraction of the iodide always dissolved towards the end of the washing. On the other hand, Werther, whilst pointing out certain erroneous facts, has not freed the question from uncertainties and difficulties which still remain entire.

A study of the question has convinced me that by observing certain rules the gravimetric determination of thallium may be effected with the greatest accuracy. Thus:—

1. Willm's complaint that the method is deficient in accuracy must be imputed solely to his method of procedure. Towards the end he washed the precipitate with distilled water, and of course dissolved some thallous iodide.

2. We must reject as erroneous Werther's assertion that this iodide is insoluble in ammoniacal water; for if it is certain that the acidity of the liquid promotes solubility, and that it is better to operate in a neutral or an ammoniacal liquid, it is no less certain that the mere presence of ammonia is insufficient to obviate the solubility of the iodide in water, and that we no more ought to complete the washing with ammoniacal water than with pure water. Further, the solubility is even increased, as it may be proved by comparative determination if to the ammoniacal solution we add a little clean ammoniacal salt, sulphate or chloride.

3. The solubility in weak alcohol is not so great as Werther alleges; for if at 13°, in alcohol at 85°, the coefficient of solubility, given by Werther $\frac{1}{354100}$, were correct, we should have 11 m-grms. metallic thallium per litre, and at this concentration alkaline sulphides would immediately give a precipitate of sulphide. But if we shake up thallous iodide, pure and recently precipitated with alcohol marking 78° at the temperature of 22° (1 vol. of water and 3 vols. of alcohol at 98°), and allow it to digest for twenty-four hours, and then reduce the filtrate to one-fifth of its value by slow evaporation, the aqueous liquor which remains is not even coloured by ammonium sulphide.

If to these data we add that thallous iodide is insoluble in a solution of potassium iodide at 1 per cent, and that potassium iodide is still moderately soluble in alcohol at 82° (4 vols. of alcohol at 98° and 1 vol. of water), we have all the conditions necessary for the total separation of thallium contained in a saline solution.

As for the precipitation, Willm recommends to effect it in the cold and to wait for twelve hours before filtering. Werther operates in heat and filters a few hours afterwards. Experience shows me that it is preferable to

operate in heat at 80° to 90°. The precipitate collects better, and the adhesion to the glass of which Willm complains is almost null. The only precaution to be taken is to filter after cooling, when the liquid is quite clear, which is accelerated by setting the beaker in cold water. The orange precipitate, very fine at first, is transformed into a yellow powder, heavy and crystalline, which passes less readily through the filters.

From these observations there results a simple and rational procedure. The thallium is precipitated in heat by an excess of potassium iodide in a neutral solution, so that the liquid after precipitation may still contain 1 per cent of the potassium iodide, which is easily effected by operating with a solution of iodide of known strength. It is filtered by decantation, and repeatedly washed with a solution of potassium iodide at 1 per cent, in order to remove foreign salts, and the washing is completed with alcohol at 80° to 82°.

The precipitate is decanted upon the filter and dried. The collected filtrates and washings, when reduced to a small volume, never showed thallium sulphide when tested with an alkaline sulphide. It is of course necessary to ascertain previously that all the metal is in the thallous state, otherwise it must be reduced to that state by a little sulphurous acid.

When the product is dried there is a further difficulty. The volatility of the thallium compounds and of the metal itself, if heated rather strongly in presence of a reducing body, *e. g.*, a filter, interferes with the incineration of the filter if we wish to avoid all loss. Hitherto a filter tared after desiccation at 100° has always been used. We know the imperfections of this method and the many uncertainties which it involves. I have therefore sought a way of escape, and have found a very simple procedure. The bulk of the thallous iodide is removed from the filter, and upon the small quantity which remains attached to the filter there are let fall a few drops of hot dilute nitric acid (2 vols. of water to 1 vol. of acid at 36°). The iodide is decomposed; it is washed in a little hot water, and all the thallium is carried away as nitrate. The liquid, collected in a small tared porcelain capsule, is gently evaporated to dryness with a few drops of HCl. The chloride formed is decomposed by a drop of a concentrated solution of potassium iodide, which converts the thallous chloride into iodide mixed with iodine from the reduction of a little thallic salt, formed in presence of nitric acid. But thallous iodide, as I have found by direct experiment, is decidedly fixed, even at 170°,—at least its weight does not vary appreciably, even after heating for several hours. The small excess of iodine is therefore expelled by heating for some hours to 170°. The thallous iodide which has been previously collected is poured into the crucible, and the whole is weighed.—*Comptes Rendus* (cxliii., Oct. 26, 1891).

EXPERIMENTS RELATING TO IMPROVEMENTS IN THE MANUFACTURE OF METALLIC SODIUM.

By H. N. WARREN, Research Analyst.

In the general process for the manufacture of metallic sodium, one of the greatest drawbacks at the present time is the difficulty of expelling the sodium as quickly as reduced in the form of vapour, inasmuch that, for a considerable time after, a most intense heat has been obtained: on viewing the inside of the converters large globules of melted sodium are not unfrequently observed, which are only with difficulty volatilised. Potassium, on the other hand, although presenting more difficulties than sodium as regards its preparation, melts and volatilises at a much lower temperature; for instance, if 23 parts by weight of sodium be carefully alloyed with 29 parts of

potassium, a fluid amalgam is produced which remains liquid at all ordinary temperatures; if this amalgam is now distilled in a non-oxidising atmosphere, in the first place potassium metal distils over, leaving a residue consisting of sodium containing about 5 or 6 per cent of potassium: this alloy, which resembles ordinary sodium in appearance, is much more energetic than that substance itself, taking fire when thrown upon the surface of water the same as potassium, but burning with the characteristic yellow flame of the former.

Following up these reactions several mixtures were obtained for reduction, by calcining sodium tartrate in admixture with a sufficiency of potassium tartrate to allow of about 5 or 6 per cent of potassium to pass into the distillate; the reaction being brought about in wrought-iron tubes, and urged to whiteness by the aid of a small blast furnace.

The globules of metal thus obtained presented in appearance an exact similitude with the first-mentioned alloy, and were considerably more volatile than pure sodium. The iron tubes after cooling were cut longitudinally, and in no instance could any reduced metal be detected; the metals as fast as reduced having been volatilised, producing the aforesaid alloy.

The calcining of tartrates on a large scale would naturally be entirely out of place; but the introduction of potassium could, as far as can be seen, be brought into play when employing any of the ordinary commercial methods, save that the percentage of the two would probably have to be looked into still closer in order to obtain concordant results.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

DETERMINATION OF SMALL QUANTITIES OF ALKALI AND RECOGNITION OF THE NEUTRALITY OF WATER.

By F. MYLIUS and F. FOERSTER.

(Continued from p. 229).

For the preparation of mille-normal solutions we must use pure or, at least, neutralised water, since otherwise the alkaline impurities derived from the glass vessels in which the water is preserved have a decidedly disturbing effect. Mille-normal solutions can be kept for some time in bottles of good glass. The titration is advantageously conducted in a small stoppered bottle, from 50 to 100 c.c. of the aqueous liquid under examination being shaken up with 10 to 20 c.c. of an ethereal solution of iodeosine containing 2 m.grms. of the colouring matter per litre. Such a solution, which appears almost colourless, can be obtained by diluting the ethereal solution of iodeosine to be mentioned below. If free alkali is present, the lower stratum, after shaking, appears rose-coloured, whilst on neutralisation with alkali it becomes colourless again. The titration is best completed by again adding so much solution of alkali that a distinct rose colour reappears. The small excess of about 2 c.c. thus produced must be deducted from the total quantity of solution of alkali consumed.

The influence of carbonic acid upon titration with mille-normal solutions, according to the process above described, is not important. Even on titration with decinormal solutions, using an ethereal solution of iodeosine, it interferes little, as is shown by the following experiment:—For neutralising 40.7 c.c. decinormal sulphuric acid, which, when tested with litmus (the carbonic acid having been previously expelled by heat), required 40.7 c.c. of a decinormal solution of sodium carbonate, there were consumed, when an ethereal solution of iodeosine was used as indicator, 41.2 c.c. of the soda solution in order to pro-

duce a distinct red colouration. Decinormal soda-lye consumed equal quantities of decinormal hydrochloric acid, whether litmus or an ethereal solution of eosine was used as an indicator. In its behaviour with carbonic acid, there is consequently a decided contrast between iodeosine and phenolphthalein, although the two differ but little in their chemical nature.

The following instances may show the varied applicability of the method:—

The carbonates dissolved in spring- or well-water may be quickly and easily determined. The acid consumed is equivalent to the "combined" carbonic acid in the water. 5 c.c. water from the Charlottenburg mains consumed for neutralisation 15.2 c.c. N/1000 sulphuric acid, which corresponds to 6.7 grms. of "combined" carbonic acid in 100,000 water. Titrations of drinking-water have been effected with centinormal solutions, using carmine as indicator.

The solubility of calcium carbonate in pure water which has been repeatedly determined can be readily shown by this method. Finely pulverised marble was well washed, and then left for some time in contact with neutral (see below) water which had been previously deprived of carbonic acid by ebullition in platinum vessels. 25 c.c. of the solution thus obtained, after the lapse of seven days, required for neutralisation 15.5 c.c. N/1000 sulphuric acid. A litre consequently contained 31 m.grms. calcium carbonate in solution. The decomposition of neutral salts of ammonium, when their solutions are heated, can be shown by means of titration with mille normal solutions. A decinormal solution of commercial crystalline ammonium sulphate in "neutral" water, which was itself neutral, was distilled in the apparatus to be described below. Appreciable quantities of ammonia were present in the distillate; 200 c.c. were three times distilled off in succession; 25 c.c. of the first distillate required for neutralisation 32.5 c.c. N/1000 sulphuric acid; the same quantity of the distillate required 34.5 c.c., and of the third 37 c.c. of the acid. Hence it appears that the concentration of the solution in the distillatory vessel increases little. The ammonia present in the 600 c.c. of water distilled was 0.01416 gm. NH_3 , i.e., 0.83 per cent of the total ammonia present.

The eosine reaction is particularly useful for testing the neutrality of salts.

If a salt is considered neutral the solution of which, on shaking with ethereal solution of eosine, is turned red by a minimum of mille-normal soda-lye, many of the salts sold as pure are not neutral. Thus, e.g., 5 grms. of Kahlbaum's sodium chloride required for the production of a red colour 1.1 c.c. N/1000 soda-lye, corresponding to the presence of 0.0008 per cent hydrochloric acid. The same preparation, after ignition, was found to be faintly alkaline, since 5 grms. required 1.4 c.c. N/1000 sulphuric acid for neutrality. As regards the alkaline sulphates, further observations are needed. We merely remark that a commercial and apparently pure specimen of potassium sulphate had a distinctly alkaline reaction.

The recognition of the neutrality of salts of the zinc group has hitherto been especially difficult, but iodeosine was here found to be the most sensitive indicator. The hydroxides of metals of the zinc group, like the alkalies and alkaline earths, form with iodeosine soluble salts of a reddish violet. In the solutions of the basic salts a red colour appears on shaking up with ethereal solution of iodeosine; but the slightest excess of free acid prevents the appearance of salts of colouring-matters.

For the production of neutral zinc sulphate, the commercial salt, having an alkaline reaction, was twice recrystallised from a carefully neutralised solution; 5 grms. of the crystals dissolved in water and shaken with ethereal solution of eosine gave a colourless solution; but 2 c.c. N/1000 alkali sufficed to produce a distinct rose colour.

(To be continued).

THE REASON OF THE SPARING SOLUBILITY OF CHEMICALLY PURE ZINC IN ACIDS.

By JULIUS M. WEEREN.

SINCE De la Rive in 1830 made the observation that chemically pure zinc is almost insoluble in dilute sulphuric acid, this puzzling and interesting phenomenon has been the subject of research, but without meeting with a satisfactory explanation. The question derives increased importance from the fact that other metals, if pure, and other acids behave in a similar manner. Nitric acid alone attacks most metals considerably, even if chemically pure.

Since it has been found that the same metals, which in a chemically pure state were almost insoluble in acids, are always more or less rapidly attacked by the same acids when impure, the attention of investigators was turned to the impurities and the adherents of the contact theory recognised in this different behaviour of the pure and the impure metals,—a defence against the attacks of the supporters of the chemical theory.

According to the contact theory the electric current arises in a closed circuit (Zn, Pt, H_2SO_4) by the origination of a difference in the electrical potential due to the contact of the two metals. This difference tends to be equalised by the acid. But as an electrolyte—in this case the sulphuric acid—cannot conduct the electric current without itself being decomposed, such a decomposition of the acid is effected by the current which passes from the zinc through the sulphuric acid to the platinum. The hydrogen is set free upon the platinum and the acid radicle, in virtue of its liberated affinities combines, with the zinc to form zinc sulphate. In brief, the contact theory views the solution of the zinc as a consequence of the electric current running from the zinc to the platinum in consequence of the electric opposition of the two metals; the zinc must remain undissolved as long as no electric difference is present. Hence impure zinc, but not pure zinc, dissolves in acids.

The contact theory thus seemed to solve the problem in a simple and natural manner, and in consequence it met with almost universal acceptance.

But this explanation did not agree with the facts that chemically pure metals are, in general, easily dissolved by dilute sulphuric acid, if boiling, as also by cold nitric acid. These reasons led me to give up the theory above given, and to seek elsewhere for the cause of the insolubility of pure metals in acids. In this investigation I ultimately succeeded and found an explanation for the phenomena at once simple and comprehensive.

I maintain that chemically pure zinc or other chemically pure metals are insoluble or sparingly soluble in acids, because at the moment of their immersion in the acid they are at once enclosed in an atmosphere of condensed hydrogen, which under normal conditions makes any further action of the acid impossible. This immeasurably thin but everywhere continuous layer of hydrogen is alone the cause of the insolubility or sparing solubility of chemically pure zinc in dilute acids.

Absolute insolubility is from various reasons out of the question if we consider that both the varying density of the surface and minimal traces of foreign metals, such as we may suppose even in chemically pure zinc, must give rise to very feeble local currents, which are of course attended with a slight solution of the zinc.

It is known that on the action of nitric acid upon the zinc there are formed, according to the concentration of the acid, NH_3 , N_2O , NO , N_2O_3 , and N_2O_4 . There is at first formed upon the zinc hydrogen, which in its nascent state is at once oxidised to water by the excess of nitric acid, whilst the latter is reduced to the above mentioned nitrogen compounds. Where then are the latter formed? Certainly not directly on the surface of the zinc, from which they are separated by that stratum of water which

has been formed by the oxidation of the nascent hydrogen. This stratum is certainly very thin, but it suffices to abolish the attraction between the metal and the gas which is formed. Zinc, therefore, on treatment with nitric acid, is never enclosed in a protective coating of gas, but it is exposed on its entire surface without protection to the attacks of the nitric acid.

The conditions of impure zinc if treated with sulphuric acid are similar. The hydrogen formed is not liberated on the zinc, but on the accompanying impurities which are more negative than zinc. Consequently the true surface of the zinc remains always free from gas, so that the action between metal and acid goes on continuously.

Similar results are obtained also with cadmium, cobalt, nickel, iron, and aluminium. Aluminium, which is otherwise scarcely or not at all attacked by dilute sulphuric or nitric acid, dissolves easily in these acids in a vacuum. It dissolves also readily in a vacuum in a perfectly neutral solution of ferric chloride which is reduced to ferrous chloride with an escape of hydrogen. At the ordinary atmospheric pressure this process is much more tedious.

It would be interesting to ascertain whether hydrogen gas alone possesses the property of condensing in its nascent state upon metals, and of thus rendering them unattackable by acids, or if this property is common to other gases. If this is not the case we are entitled to assume that in these phenomena of adhesion the metallic character of hydrogen plays a part of greater or less importance, and that we have here a transition to the compound of palladium and hydrogen.—*Ber. Deutsch. Chem. Gesell.*, vol. xxiv., p. 1785.

ELECTROLYTIC DETERMINATION OF METALS AS AMALGAMS.*

By G. VORTMANN.

(Continued from p. 228.)

Determination of Zinc.

IN 1885 C. Luckow recommended the separation of zinc as amalgam from a weak sulphuric solution. I can confirm the accuracy of his statement, but a large excess of free acid may completely prevent the separation. I therefore preferred to undertake the precipitation of the zinc from the solution of the double ammonium oxalate or from an ammoniacal solution.

1. *Separation of Zinc from the Solution of the Double Oxalate.*—The zinc salt along with a weighed quantity of mercuric chloride was dissolved in water in a platinum capsule and mixed with an excess of ammonium oxalate (3–5 grms.). On electrolysis the zinc amalgam was deposited upon the platinum capsule as a silvery white layer and could be washed without loss. To ascertain whether the precipitation was complete a portion of the liquid was tested with ammonium sulphide. The mercury must not be in too large a proportion to the zinc (to one part zinc not more on the outside than 2–3 parts mercury), as the zinc is otherwise deposited in a spongy form. Moreover zinc is easily deposited without mercury, the addition of which has merely the purpose to facilitate the removal of the deposit from the platinum capsule. Like the other amalgams zinc amalgam does not require to be transferred rapidly to the balance, as it neither loses nor gains weight if left in the exsiccator for a considerable time.

2. *Separation of Zinc from an Ammoniacal Solution.*—The precipitation of zinc as an amalgam from an ammoniacal solution containing tartaric acid takes place similarly to that from the double oxalate; a larger quantity of mercuric chloride must, however, be used (to 1 part zinc at least 3 parts of mercury), as the amalgam otherwise falls off in scales. A large excess of mercury is in this case not hurtful.

* *Berichte Deutsch. Chem. Gesell.*

The amalgam, whether deposited from solution of ammonium oxalate or from an ammoniacal liquid, is readily dissolved by dilute nitric acid; there remains a black powder consisting of platinum black which adheres to the capsule but is easily removed by friction. If the capsule is weighed after removal of the zinc amalgam, rinsing with alcohol and ether, and desiccation, it has its original weight, or it weighs only 1—2 m.grms. more than before the electrolysis. After the removal of the black powder, the weight of which is sometimes very appreciable, the loss of weight of the capsule is sometimes only a few m.grms., but occasionally may reach 5 centigrms. On account of this loss of weight the separation of zinc as amalgam cannot be recommended, and the previous method, according to which the capsule is first coated with copper or silver, is to be preferred.

Determination of Cadmium.

Cadmium, like zinc, can be separated as an amalgam, either from the solution of the double ammonium oxalate or from an ammoniacal solution. The latter is more uniform if the mercury is present in large excess (at least 4 parts to 1 part of cadmium); if but little mercury is present the amalgam separates in a crystalline form and does not adhere sufficiently to the platinum, so that it cannot be easily washed without loss. If the amalgam contains 4—6 parts of mercury to 1 part cadmium, it is so hard that it may be rubbed with the finger without removing any portion. If the quantity of the mercury is eight times as large as that of cadmium, the amalgam is in part liquid. It does not become oxidised in the air, and can be preserved for several days without any change in its weight. Dilute nitric acid dissolves it readily, and as a rule, without a residue of platinum black; rarely is a faint blackness perceptible.

As cadmium ammonium oxalate is less soluble in water than the corresponding zinc salt, and as a larger quantity of mercuric chloride must be dissolved, the oxalate method is suitable only for the separation of small quantities of cadmium (about 0.2—0.3 grm.).

The solution containing the salt of cadmium and the mercuric chloride is mixed with about 5 grms. ammonium oxalate, stirred up, and diluted as far as possible with water. The ammonium oxalate must be dissolved in the cold, as on the application of heat a precipitate of mercurous chloride may be produced in a concentrated solution.

If the quantity of cadmium exceeds 0.3 grm. an ammoniacal solution must be used. In this case the solution of the cadmium and the mercuric salt is mixed with about 3 grms. tartaric acid and then with ammonia until it smells strongly, diluted with water, and exposed to the electric current until a portion of the liquid is not rendered turbid by an addition of ammonium sulphide.

Determination of Lead.

1. *Separation of Lead from Acid Solutions.*—In the determination of lead as an amalgam, I encountered difficulties, as the lead was partly separated out at the positive electrode as a peroxide, and cannot be removed readily by reducing agents, or, in some cases, not at all. Tartaric and oxalic acids, ethylic alcohol, potassium iodide had little effect. The removal of the lead peroxide was best effected by means of nitrous acid. I dissolved the lead salt and the mercuric chloride in water; adding 3—5 grms. sodium acetate and a few c.c. of a concentrated solution of potassium nitrite. The white precipitate formed was dissolved in acetic acid. The clear yellow solution thus obtained was submitted to electrolysis. As long as the liquid contained nitrous acid, no lead peroxide was formed, but towards the end of the process there appeared on the positive electrode a brown stain, which quickly disappeared on the addition of a few drops of solution of potassium nitrite. When a portion of the liquid gave no colouration with ammonium sulphide, the liquid was decanted off, the lead amalgam was

rapidly rinsed with water, alcohol, and ether, quickly dried by warming the capsule in the hand whilst a current of air is directed upon it, and then placed in the exsiccator.

The lead amalgam, when dry, is permanent in the air, and does not vary in weight if it remains for twenty-four hours in the exsiccator. In a moist state, it is readily oxidised; hence, after rinsing with water, that liquid must be removed as quickly as possible with alcohol and ether. Oxidation, however, is not so rapid as to render the determinations inaccurate; the moist amalgam undergoes no change for about five minutes. It then gradually loses its lustre, and is coated with a yellowish white film. It is readily soluble in nitric acid, and leaves on the platinum capsule a very faint stain of platinum black.

The separation of lead as amalgam can also be effected in an aqueous solution acidulated with dilute nitric acid, to which a little potassium nitrite is added in order to prevent the formation of lead peroxide. As the quantity of nitrite which a liquid containing free nitric acid can take up without a violent escape of nitrous acid is very trifling, there is formed at the positive electrode during electrolysis a thicker layer of lead peroxide than in an acetic solution. It must be re-dissolved by the frequent addition of a few drops of the solution of potassium nitrite. The analysis is in this case more tedious than with an acetic solution, and must be continued until no more lead peroxide is deposited at the positive electrode, and until no lead can be detected in the liquid by means of ammonium sulphide.

The determination of lead as amalgam has the advantage of being applicable to larger quantities of the metal than the process at present in use.

(To be continued).

DETERMINATION OF MANGANESE IN MANGANIFEROUS SLAGS AND ORES.

By G. L. NORRIS, Pencoyd, Pa.

THE manganese in slags from blast furnaces making spiegel, and in open hearth slags, is easily and rapidly determined in the following way:—

One grm. of the finely powdered slag is placed in a 4-ounce Griffin beaker, moistened slightly with water to prevent caking, and 50 c.c. of nitric acid of 1.42 sp. gr. added. Bring to a boil, and while the slag is in suspension add 3 or 4 c.c. of hydrofluoric acid. The slag is rapidly decomposed and the silica driven off. Boil the solution for a few minutes to drive off any remaining hydrofluoric acid, then transfer to a larger beaker or a precipitating flask, add more nitric acid, bring the solution to a boil, and precipitate the manganese with potassium chlorate. Filter off the manganese dioxide upon an asbestos filter. The manganese dioxide may either be dissolved in standardised oxalic acid or ferrous sulphate solution, and the excess of the solvent titrated with permanganate of potassium, and the amount of manganese calculated; or the manganese may be finally weighed as the pyrophosphate.

For manganese in ores:—1 grm. or 0.5 grm., according to richness of the ore, is placed in a 4-ounce Griffin beaker, moistened with water, and 50 c.c. nitric acid of 1.42 sp. gr. added. Bring to a boil and add a few small pieces of tartaric acid. Ores made up largely of the mixed oxides of manganese go into solution readily. When the solution clears, add a little hydrofluoric acid to decompose the residue. Where there is much oxide of iron in the ores it is better to add the hydrofluoric acid along with the tartaric acid.

Drive off any remaining hydrofluoric acid, and be sure that the tartaric acid is all decomposed. Add more nitric acid, boil, and precipitate the manganese with potassium chlorate.

The nitric acid breaks up all the other oxides of manganese into the oxide and dioxide, and dissolves the monoxide, while the tartaric acid causes the solution of the dioxide. Considerable tartaric acid may be used, as it is readily decomposed by boiling in the nitric acid solution.

By this method the manganese can be determined in about forty-five minutes, while a much longer time is required by the ordinary way of solution in hydrochloric acid, with separation and fusion of the residue and consequent accumulation of salts.—*Journal of Analytical and Applied Chemistry*, August, 1891.

A METHOD OF OBTAINING AMMONIA-FREE WATER.

By D. B. BISBEE.

A VERY easy way of obtaining ammonia-free water, which I have used for some time and have never seen mentioned, is to acidulate the water, before distilling, with sulphuric acid. The acid holds all ammonia in the retort, the first portions even of the distillate being ammonia-free. But this acidulation naturally causes the nitric and nitrous acids in the water to distil over. For some purposes, however, nitrates are not objectionable. At the laboratory of the Iowa Agricultural Experiment Station, Ames, Iowa, when we wish to obtain chemically pure water for any use, we take distilled water, which is nitrate-free, acidulate with sulphuric acid, and distil, at once getting pure water.—*Journal of Analytical and Applied Chemistry*, August, 1891.

THE USE OF CADMIUM IN ASSAYING GOLD BULLION.*

By CABELL WHITEHEAD,
Assayer to the Mint Bureau.

CADMIUM, as a substitute for silver in assaying gold bullion, was first used by Balling (Crookes's "Select Methods in Chemical Analysis"). He states that the gold is entirely parted from all metals, except the platinum group, when its alloy with cadmium is boiled with strong nitric acid for one hour, followed by a second boiling for ten minutes with fresh portion of same acid. For general assays of gold bullion I do not think that Balling's method with cadmium will bear comparison in point of accuracy with the old one of quartation with silver and cupellation. But, with certain modifications which will be suggested later, it will be found rapid and satisfactory for a preliminary assay.

It is, however, in the estimation of small quantities of silver in gold bullion containing considerable amounts of copper or platinum, that I have found cadmium to be a most efficient aid.

The difficulty in determining silver in the presence of platinum by cupellation is well known to assayers. In such cases the following has been the method in the United States Mint at Philadelphia:—

An approximate assay is made by cupellation, after which, and based on this approximation, enough pure silver is added to 500 m.grms. of the bullion to make in all at least 1004 m.grms. of silver present in the assay. This weighed silver and bullion is wrapped in a sheet of lead weighing 2.5 grms., and the whole placed on a hot cupel in the muffle furnace.

As soon as the lead "clears" the cupel is withdrawn; when cold the button is flattened and put in a bottle such

as is used in the humid assay of silver, dilute nitric acid is added and heat applied. When action ceases, the silver present in solution is determined volumetrically as usual. The silver found, less the amount added, gives the silver in 500 m.grms. of bullion.

There are two objections to this method: (1) The insolubility of lead nitrate in nitric acid necessitates the use of dilute acid, which leaves much alloy with the gold; (2) the alloy to be removed is one-third silver. This is very important when small quantities of silver are to be determined, as in the case of gold coin, which rarely contains more than 0.003. Cornets, after three boilings with acid (ten minutes each), retain from 0.002 to 0.0025 of silver; so it will be seen at a glance that the amount retained after one boiling with dilute acid will be much greater, and the gold residue will contain more silver than was present in the original bullion.

The presence of 10 per cent or more of copper in high grade gold bullion makes the accurate determination of silver by cupellation impossible. Not only is gold taken into the cupel in large quantities by the copper, but it is also left in specks over the entire surface covered by the assay, thus making a "proof" practically worthless.

The method which I am about to describe was devised for the estimation of silver in gold coin, and has been in use in the laboratory of the Bureau of the Mint for the past year, where it has given such satisfactory results that it is thought a brief description may prove of interest to others engaged in the same line of work.

Five hundred m.grms. are weighed into a porcelain crucible and covered with 10 grms. of potassium cyanide. The potassium cyanide is melted over a Bunsen burner or preferably a blast lamp. When the cyanide is in quiet fusion 1 grm. of cadmium is dropped into the crucible, where it quickly melts and forms a bright, homogeneous alloy with the gold. After gently shaking, so as to bring the cadmium in contact with every particle of bullion, the crucible is removed and the contents poured on a clean porcelain slab, where it soon solidifies. The alloy will be found in one piece and is easily detached from the potassium cyanide. It is now washed in warm water, dried, and placed in a diamond mortar, when several sharp blows with a hammer quickly reduce it to powder.

This powder is carefully transferred to an assay bottle, 1004 m.grms. of pure silver added and 10 c.c. of nitric acid—32° Baumé—poured on. In from five to ten minutes (depending upon the heat used) the solution is complete and all action has ceased. The bottle is now cooled and 100 c.c. of normal salt solution is charged and the bottle shaken. The precipitation is finished with the decinormal solution.

This assay is accompanied by another called a "proof," made of 1004 m.grms. of pure silver dissolved in the same amount of acid. Now the excess of silver found in the assay, over that shown in the "proof," is the amount contained in 500 m.grms. of coin. This doubled gives parts of silver per thousand.

Example:—An alloy composed of 499 m.grms. pure gold, 1 m.grm. of silver, and 1 grm. of cadmium, treated as above described, after being charged with 100 c.c. normal salt solution, required 5 c.c. decinormal solution for complete precipitation of the silver present. A proof assay, carried along as check, upon 1004 m.grms. of pure silver, required in addition to 100 c.c. of normal salt solution, 4 c.c. of decinormal solution for complete precipitation = to 1004 c.c. decinormal solution. Hence, each c.c. decinormal equals 1 m.grm. silver, and 1 c.c. decinormal solution required by the bullion, in excess of that called for by the silver added, shows the bullion to contain 1 m.grm. silver in 500, or 2 parts per 1000.

It may be asked by those not familiar with mint appliances and usages, "Why not titrate directly the silver brought into solution with the cadmium instead of adding a known weight of pure silver and finding the desired result by difference?"

* A communication to the Chemical Section of the Franklin Institute, Sept. 15, 1891.

The reply is that the small amount of silver present in this class of bullion would, as chloride, not "clear" on shaking, and much time would be consumed in finding the end reaction. By the method described the usual apparatus and solutions may be availed of and results rapidly obtained.

When no such reasons exist the sulpho-cyanide method alluded to at the end of this article is recommended.

Example in Gold Bullion.

An approximate assay gives by cupellation 0.035 silver, hence 500 m.grms. will contain about 17.5 m.grms. of that metal, and 986.5 m.grms. must be added to bring the total silver up to 1004 m.grms. If copper is not present about 50 m.grms. is added, it being found that the alloy of copper with cadmium is very brittle, and the resulting button is easily crushed to powder.

The sample having been fused with cadmium in presence of potassium cyanide is powdered and subjected to treatment with nitric acid as above described.

After charging with 100 c.c. normal salt solution, and shaking, the assay required 4.5 c.c. decinormal solution for end reaction. A "proof" consisting of 1004 m.grms. pure silver in solution, treated in same manner, required but 3 c.c. decinormal solution.

Hence the assay contained $4.5 - 3 = 1.5$ m.grms. more silver than the proof, or $1004 + 1.5 = 1005.5$ m.grms. in silver in all. This, less the 986.5 m.grms. silver purposely added, gives 19 m.grms., as the silver present in 500 m.grms. of bullion taken, or thirty-eight parts in each thousand instead of thirty-five parts found by cupellation.

In favour of the new method it may be said—

(1) That the ready solubility of cadmium in nitric acid of any strength makes it possible to dilute (if the term may be used), the silver present in gold bullion, to any desired extent, while, on the other hand, the difficult solubility of lead necessarily limits the dilution possible by the time required for its even imperfect extraction.

The inevitable small portion of other metals retained by the gold after treatment with nitric acid may therefore, by the use of cadmium, be made to contain but an infinitesimal quantity of silver.

(2) The brittleness of the button obtained permits it being crushed to a powder, in which condition the alloy rapidly yields its soluble portion to nitric acid, and the time required for an assay is materially shortened.

(3) The low temperature required enables the chemist to dispense with all special appliances. A Bunsen burner will well answer the requirements for heating purposes, and little more is needed beyond a standard salt solution. No muffle or rolls are wanted.

In a laboratory where few assays are made the following method might be followed and very satisfactory results obtained. After alloying and crushing, treat in a parting flask with 15 c.c. of nitric acid, 32° Baumé, for ten minutes; pour off this acid into a beaker, add 15 c.c. acid same strength and boil for ten minutes longer, pour off again in same beaker, wash with hot water and take out in an annealing cup, dry and heat over blast lamp, weigh and deduct 0.25 m.grm. for cadmium retained. Twice this weight gives the gold fineness.

The acid and washings are evaporated to drive off free nitric acid, and silver determined either as chloride, or volumetrically with sulphocyanide with ferric indicator. Cadmium nitrate does not interfere in the least with determination of silver, either as chloride or as sulphocyanide.

Detection of Paraphenetidine in Phenacetine.—L. Reuter.—The author introduces 0.5 grm. of the specimen into 2.5 grms. of melted chloral hydrate and mixes. If the phenacetine is pure the solution is clear and colourless. But mere traces of paraphenetidine colour the solution at once of a more or less intense violet.—*Zeitsch. f. Anal. Chem.*, xxx., Part 3.

ON THE OCCURRENCE OF NITROGEN IN URANINITE, AND ON THE COMPOSITION OF URANINITE IN GENERAL.*

By W. F. HILLEBRAND.

(Continued from p. 233.)

Detection and Examination of Nitrogen.

At an early stage in the work it was noticed in a few instances, where the sealed tubes in which UO_2 was to be estimated were left in an upright position for a short time, that an extremely slow disengagement of gas took place, which was especially noticeable if the tubes were gently tapped on the table occasionally, whereby the bubbles enmeshed by the powder were set free and rose through the liquid in the tube. This was supposed to be due to the presence of traces of carbonates in the mineral, and no particular attention was paid to it, although it seemed strange that they should not be entirely decomposed in a very few moments after contact with the acid. Later, when making the first estimation of UO_2 in Glastonbury uraninite above mentioned with hydrofluoric acid, solution in this case being made in the cold and with free access of air, it was observed that this slow escape of gas was continuous throughout the whole ten days required for decomposing the mineral. This seemed to exclude the possibility of its being carbonic acid, and it was determined to collect and examine it if possible. This was done in a manner to be hereafter described.

It may be here mentioned that U_3O_8 and UO_2 prepared from the residues obtained during this work, when examined under conditions precisely similar to those obtaining with uraninite, failed to give off the least trace of gas.

The gas was colourless, odourless, a non-supporter of combustion, unchanged by mixture with air, neutral to moistened litmus papers, not absorbed by caustic alkalis, and insoluble in water; at least its coefficient of absorption was so small as to be inappreciable without elaborate experimentation.

In a Bunsen's absorption tube, containing gas from the original bröggerite, a potash ball caused no diminution in volume, neither did potassium pyrogallate, thus showing the absence of carbonic acid and of oxygen. Transferred from the absorption tube to a eudiometer, the gas was then subjected to the tests prescribed by Bunsen ("Gasometrische Methoden," 2nd ed., pp. 73, 74.

	Unim.
Reduced initial volume	14.01
After exploding with oxyhydrogen	13.21
After a second similar treatment	13.20
After addition of hydrogen (32.79)	45.99
After explosion with oxyhydrogen	45.93
After addition of air in excess	181.82
After exploding	132.81
Contraction	49.01

Two thirds of which, or 32.67, is almost exactly the volume of the hydrogen introduced. Were it not for the relatively large contraction after the first explosion, 0.80 units, representing 5.71 per cent of the initial volume, the above tests would indicate almost incontestably that the gas could be nothing but nitrogen. Considering the small volume operated upon, and the great disadvantages under which the eudiometric experiments were made, the above is not a surprising error, and, since in other experiments it did not recur, I have no hesitation in regarding it as without significance.

Gas liberated from bröggerite by hydrochloric acid had, after treatment in the absorption tube, in the eudiometer,—

* From "Bulletin No. 78, U.S. Geological Survey, 1889—90." An abstract of this paper was published in the *Am. Jour. Sci.*, vol. 34, p. 384.

	Units.
A reduced initial volume of	27.73
After addition of hydrogen (25.77)	53.50
After exploding with oxyhydrogen	53.17
After addition of air	178.08
After exploding	138.20
Contraction	39.88

Two-thirds of which, or 26.58, is sufficiently close to the volume of hydrogen added to show the purity of the gas.

Gas evolved from Branchville uraninite by sulphuric acid gave in the eudiometer—

	Units.
An initial volume of	17.98
After exploding with oxyhydrogen	18.11
After addition of hydrogen (20.37)	38.48
After exploding with oxyhydrogen	37.36
After addition of air	106.32
After exploding	77.74
Contraction	28.58

Two-thirds of which, or 19.05, is nearly that of the hydrogen introduced. The admission of a trace of air into the eudiometer with the gas, or later with the hydrogen, would account for the slight contraction after the second explosion, and for the deficiency in the observed over the calculated final contraction. But such an assumption is hardly necessary, for the final readings on the eudiometer tube were very uncertain.

The evidence as to the nature of the gas, while fairly conclusive, was thus far purely negative. Proof of a more positive character was needed, and this was sought in various ways.

Long-continued passage of the electric spark between the platinum wires of the eudiometer, in which was a mixture of the gas with pure oxygen, produced a marked contraction, and a few drops of water purposely introduced above the mercury before turning on the current gave—when taken out and tested with diphenylamine, and brucine—intense blue and red colours, respectively. Blue litmus paper was turned red by it. When the terminals of a Ruhmkorff coil were connected with a simple modification of Siemens's induction tube, devised for the employment of small quantities of gas, containing a mixture of the gas with 3 volumes of electrolytic hydrogen, a slow but constant contraction resulted, provided that the product of combination as fast as formed could be removed by water or an acid. A strip of moistened red litmus paper suspended in the apparatus turned deep blue, and water used as an absorbent gave a strong alkaline reaction with litmus, besides affording with Nessler's reagent the characteristic ammonia reaction in a marked manner. With a dilute hydrochloric acid as an absorbent there was obtained 0.0190 grm. of ammonium-platinic chloride, which when heated with sodium hydrate gave off a strong ammoniacal odour, and a strip of red litmus paper held above the mixture was instantly turned deep blue. The nitrogen calculated from the above weight of $(\text{NH}_4)_2\text{PtCl}_6$ is 0.00121 grm., or nearly 1 c.c. at 0° C. and 760 m.m. The roughly measured contraction of the mixed hydrogen and nitrogen gases was in accordance with this determination. It should be hardly necessary to say that all these chemical tests were duplicated simultaneously in blank.

In a Geissler tube, under a pressure of 10 m.m. and less, the gas afforded the fluted spectrum of pure nitrogen as brilliantly and as completely as was done by a purchased nitrogen tube. In order that no possibility of error might exist, the tube was then reopened and repeatedly filled with hydrogen, and evacuated until only the hydrogen lines were visible. When now filled with the gas and again evacuated the nitrogen spectrum appeared as brilliantly as before with the three bright hydrogen lines added.

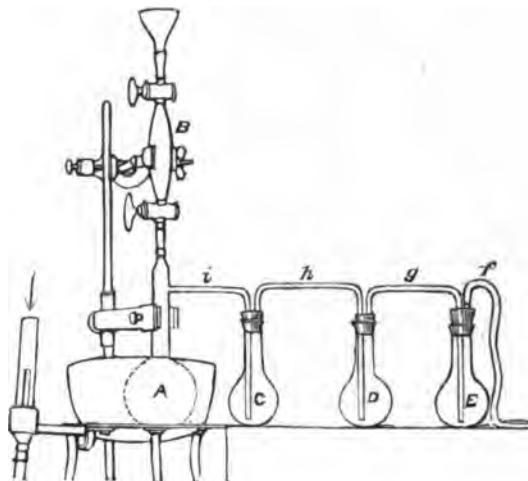
The success of these electrical experiments with Geissler and Siemens tubes is very largely due to Dr.

William Hallock, of the physical laboratory of the Geological Survey, for whose ever ready assistance and ingenuity in meeting difficulties I cannot too strongly express my appreciation.

Estimation of Nitrogen.

The original apparatus for collecting the gas is depicted in the accompanying figure.

The decomposing vessel, A, is simply a fractional distillation flask of not more than 100 c.m.³ bulb capacity, drawn out at the top to allow of connection by means of rubber tubing with the receiver B, which should approach the cylindrical in form, be provided with two closely-fitting wide-bore stopcocks, and have a capacity of 25 to 30 c.m.³. The very fine powder having been introduced into A and boiled with a few cubic centimetres of water to expel air, connection is made with B by tubing firmly wired, the receiver is suitably supported by a clamp so that A shall have the position given in the as yet empty water-bath, and the flasks C, D, E are placed in position, fitted with corks and tubes as represented, but not yet closed by the corks. A rubber tube being now attached



to B at the top, a thoroughly boiled sulphuric acid having the strength of that used for UO_2 estimations—



is poured into C, and continuously sucked into A and then into B until the latter is full above the upper stopcock, when this is instantly closed. C is then filled up with the same acid, and the water-bath with water to relieve somewhat the strain on the rubber connection between A and B. B and D are now filled with freshly boiled distilled water, and the cork of E is pressed down. Then by blowing in at F the air in G is expelled, and D can be corked without retaining the least bubble of air. By continuing the blowing H may be freed from air and C tightly corked. A may now be clamped in position for greater security, and a tin cover provided with a slit for the neck of A placed over the water-bath. This is primarily to prevent the action of steam on the rubber connection between A and B, by which after several days it is softened and injured, and secondarily to economise heat. On top of B is attached a small short-stemmed funnel, which is kept filled with distilled water, in order to insure a water seal about the stopcock and certain exclusion of all air. Heat is now applied to the water-bath, which is provided with a constant level arrangement and flow of water, so that it may be heated night and day without interruption. Soon an evolution of gas begins, the bubbles rise through A and the lower stopcock into B, and continue until the

mineral is entirely decomposed. The fine powder which is carried up into B by the bubbles may be in great measure returned to A by tapping B, and if not it is decomposed by the moderately warm acid in B, especially in case a readily soluble uraninite is being treated. The tube i should be very nearly horizontal, in order to prevent any of the powder reaching c as it falls from B. What little may collect along i itself will decompose in time, and the gas from it reach B. The outlet tube of E not being closed, free movement and escape is afforded for water in E as acid in B is displaced by gas. C, D, and E likewise act as checks to the diffusion of air into B. One or at most two flasks would suffice where readily soluble uraninites are treated, and the duration of the experiment is at most twelve hours, but for refractory varieties a third is indispensable. The greatest difference exists between North American and Norwegian uraninites as to their solubility in sulphuric, hydrochloric, hydrofluoric, and even nitric, acids. Whereas the Colorado and both Connecticut uraninites are not entirely decomposed by nine days' continuous treatment at 100° C. with dilute sulphuric acid in the above-described apparatus, and even the much altered North Carolina mineral requires five days for solution, all the Norwegian specimens examined are completely attacked in much less than twelve hours, and one (from Arendal) in three. Hydrochloric acid was used in one instance in place of sulphuric in the apparatus and with about the same effect.

When no gas is any longer given off the mineral is decomposed, as may be seen by removing the water from the bath and examining the residue in the bottom of the flask. It is either pure white sulphate of lead, or dark coloured if columbite was mixed with the uraninite. Owing to the large volume of acid used there is no separation of insoluble uranium or thorium salts as in the UO_2 estimations.

When the operation is ended B is disconnected from A after closing the lower stopcock, and the gas can then be readily transferred to a graduated and rather narrow measuring tube, or it can be measured in the receiver itself, if this is graduated, by opening the lower stopcock under water and allowing the latter gradually to displace the acid in order that the vapour tension of pure water may prevail. All necessary thermometric and barometric readings having been made, the volume in cubic centimetres is reduced to 0° C. and 760 m.m., and multiplied by the weight of 1 c.c. (0.001256 grm.) of nitrogen, in order to obtain the weight whence the percentage is obtainable.

The error due to absorption of a portion of the gas by the acid liquid, or by the water with which it is displaced in measuring, is a vanishing quantity, because of the high temperature of the acid at the time of disconnecting and the low coefficient of absorption of both liquids for the gas. If transferred from the receiver to a measuring cylinder the gas comes into contact with so much water that the element of absorption might have slight effect were time enough allowed; but the water levels within and without the measuring vessel having been brought into approximate accord, the temperature of the gas is reduced in a very few moments to that of the water by allowing a running stream of the latter to impinge on the top of the vessel and flow down on all sides, a thermometer being fastened thereto by a rubber band.

If necessary to use the solution for the titration of UO_2 , disconnection of the apparatus and transfer of the gas can be so carried out that the result of titration is very nearly as exact as by the method already described.

The above described apparatus is well enough adapted for the estimation of nitrogen in readily decomposable uraninites, and admits of constant observation of its rate of evolution; but if the heating is continued beyond a few days, the glass of that portion of the decomposing flask under water becomes devitrified and more or less cracked. This does not necessarily prevent several days' further heating, but the danger of breakage is consider-

able. Moreover, but one experiment can be conducted at a time unless several sets of apparatus are available. Therefore recourse was had, in many cases, to decomposition in sealed tubes, exactly as described for UO_2 determinations, larger quantities up to 1 grm. of mineral being used, however, and the heating prolonged, if necessary, for two or three days, to secure complete decomposition. After opening the tubes under water, the gas was at once transferred by displacement of water to a test-tube not too large to be closed by the thumb, a piece of potassium hydrate was rapidly inserted, the thumb placed over the mouth of the tube, and the latter agitated under water to dissolve the alkali and secure absorption of the carbonic acid. This was effected in a few moments, when pure water was allowed to displace the potash solution, and the gas was then transferred to the graduated tube and measured as before.

While the two methods of obtaining the nitrogen by decomposing with an acid gave pretty satisfactory results, it was desirable to estimate it by an entirely different process if possible. Fusion with alkaline hydrates produced no perceptible evolution of ammonia, and a quantitative combustion of bröggerite, mixed with sugar by the soda-lime method and absorption of any ammonia by hydrochloric acid, furnished an amount of $(\text{N}_4)_2\text{PtCl}_6$, representing but 0.03 per cent of nitrogen. Fusion with alkaline carbonates, however, liberated nitrogen gas, and furnished a means of estimation that compared well with the acid method. The process was conducted as follows:—

The substance mixed with sodium-potassium carbonate, in a porcelain boat inclosed in a cylinder of platinum-foil open at both ends, was introduced into the rear end of a combustion tube already containing a considerable layer of copper oxide in the centre, followed by 8 inches of copper gauze plugs toward the front end. To the rear was attached a tube filled with manganese carbonate, and to the front a nitrometer containing potassium hydrate solution.

Repeated heating and cooling of the copper oxide and copper in a continuous current of carbonic acid having reduced the gas unabsorbable by the alkali solution to the smallest possible limit, heat was applied under the boat. The evolution of gas began long before incipient redness, and had to be soon checked by regulation of the temperature. Finally the heat was raised to fusion, and maintained there till the absorption of gas bubbles by the alkali was as complete as before beginning the experiment. The gas was then measured and reduced to 0° C. and 760 m.m., with due regard to the vapour tension of the alkali solution, Kreussler's (*Zeit. f. Anal. Chem.*, 1885, xxiv., 445) table being used in this connection.

Of course the small quantity of nitrogen from which it is impossible to free the carbonic acid, even in a blank experiment, and which cannot be allowed for with accuracy because it may vary slightly in each experiment, produced an uncertainty in the readings of the nitrometer, but one of very slight importance, since an admixture of even $\frac{1}{4}$ a c.c. of such nitrogen could affect the result by about 0.06 per cent at the most when 1 grm. of mineral had been used. The platinum cylinder is a very necessary shield to prevent spattering of the contents of the boat on to the glass tube.

By this fusion in carbonic acid the lead contained in uraninite is apparently entirely reduced to the metallic state, and collects in globules. This reduction is probably caused by the UO_2 of the mineral, notwithstanding the fact that litharge is not reduced when thoroughly mixed with U_3O_8 or UO_2 and fused with sodium-potassium carbonate, under the conditions of the above experiment and for the same length of time. In the one case 2 molecules already existing must be torn asunder in order to admit of a re-arrangement of their constituent atoms, while in the other these constituents are assumed to exist already united in a single molecule, and in the moment

of its breaking up are most favourably situated for re-arrangement.

Nitrogen obtained in this way from Glastonbury uraninite was submitted in the eudiometer to the same ordeal as that obtained by acid, with the following results:—

	Units.
Reduced initial volume	84.69
After exploding with oxyhydrogen	84.95
After addition of hydrogen (29.02)	113.97
After addition of oxygen (25.12)	139.09
After exploding	94.40
Contraction	44.69

Two-thirds of which, or 29.79, is nearly the volume of hydrogen added. The gas then is the same as that disengaged by acids.

(To be continued.)

PROPERTIES OF PRECIPITATES, &c.*

By E. WALLER, Ph.D.

(Continued from p. 230).

H_2TiO_3 or Titanic Acid.

Rem.—Two forms, one tolerably easily soluble in acids, the other insoluble, except in very strong acids or by fusion, are known to exist. The "insoluble" form is obtained by boiling the solution acid with sulphuric. The small amounts of phosphoric acid present in iron ores and other minerals interfere somewhat with the complete separation on boiling.

Cond.—Dilute solution containing but little free H_2SO_4 . HCl and chlorides should be absent. Long boiling is necessary, the bulk of the solution being maintained. Fe, if present, should be in the ferrous form. $HC_2H_3O_2$ favours the precipitation. The best conditions for the separation of titanic acid are boiling an acetic acid solution reduced by SO_2 .

Sol.—The soluble form is attacked by the same solvents as $Fe_2(OH)_6$. The "insoluble" form is slowly soluble in hot concentrated HCl or H_2SO_4 , or by fusion with $KHSO_4$.

Contam.— Fe_2O_3 , Al_2O_3 , SiO_2 , and P_2O_5 . Some iron inevitably is converted to Fe_2O_3 , and separates with the precipitate. By re-solution, reducing, and re-precipitation, almost all can be removed. Al_2O_3 is prevented from contaminating the precipitate by the larger proportion of free acid. SiO_2 may be expelled after ignition by treating with HFl (or NH_4Fl) and H_2SO_4 . P_2O_5 by fusion for some little time, with Na_2CO_3 , and washing with dilute Na_2CO_3 solution, which leaves behind Na_2TiO_3 , soluble in acids.

Ign.—Converted to TiO_2 . Retains some SO_3 ; removable by adding a few pieces of solid ammonium carbonate and re-igniting. Volatilised by ignition with HFl, alone or with an insufficient amount of H_2SO_4 .

$(xNa_2O, TiO_2)Na_2TiO_3$. Sodium Titanate.

Rem.—Usually obtained by fusing material containing TiO_2 and P_2O_5 for some time, to convert them into sodium salts, and then to separate them by lixiviation. Chiefly of service as a step in the determination of phosphorus in titaniferous ores.

Cond.—Long fusion at a fairly high temperature is necessary. A repetition of the fusion of the portion insoluble in water, with a fresh lot of sodium carbonate, is at least necessary in order to prove the efficiency of the first fusion.

Sol.—Dissolved by acids; to some extent by water alone. Insoluble in solution of Na_2CO_3 . The washing (leaching) of the insoluble portion should be continued until the washings begin to run cloudy.

Contam.—As usually applied to iron ores or precipitates from solutions thereof, the insoluble residue may contain besides sodium titanate, Fe_2O_3 , acid sodium silicates, alkaline earth carbonates, &c.

$2ZnCO_3 \cdot 3Zn(OH)_2$. Basic Zinc Carbonate.

Rem.—Usual precipitant, Na_2CO_3 . Flocculent at first, becoming more granular by boiling.

Cond.—Solution should not contain caustic or bicarbonated alkalies or any ammonia salts. If CO_2 is evolved by addition of the reagent, it must be boiled out. Only fixed alkalies besides the zinc should be present.

Sol.—Dissolved by dilute acids, fixed caustic alkalies, bicarbonates, and ammonia salts; also by organic solutions. A very large excess of fixed alkaline chlorides hinders or partially prevents the precipitation. Insoluble in water and small amounts of fixed alkaline carbonates.

Contam.—Alkaline carbonate, necessitating several washings by decantation with boiling water to remove it. Fe_2O_3 , Al_2O_3 , SiO_2 . By dissolving the precipitate in HCl after ignition, Al_2O_3 and SiO_2 are left insoluble; on precipitating the solution with ammonia, re-dissolving and re-precipitating two or three times, $Fe_2(OH)_6$ is separated. These impurities may then be ignited, weighed, and deducted.

Ign.—Converted to ZnO , which in itself is not volatile. In contact with C or reducing substances, metallic zinc which is volatile may be formed.

$ZnNH_4PO_4$.

Rem.—Usual precipitant, $NaNH_4NPO_4$. Some prefer Na_2HPO_4 in presence of ammonium salts. The best method of procedure is to add the alkaline phosphate to the acid solution and then to neutralise the hot solution by adding ammonia, little by little, finally to heat, immersing the beaker in a boiling water bath until free NH_3 is expelled and the precipitate is crystalline. The solution containing the precipitate cannot be boiled without bumping vigorously. The precipitate can be dried at 100° and weighed as $ZnNH_4PO_4$, or ignited and weighed as $Zn_3P_4O_{17}$.

Cond.—Oxalates should be absent. Large excess of ammonium chloride or acetate should be particularly avoided. Practically, the solution should only contain alkalies besides the zinc.

Sol.—Dissolved by acids, excess of ammonia, ammonium oxalate, chloride, or acetate, especially if hot. The solvent effect of the chloride and some other ammonium salts is to a very great extent diminished by the use of an excess of alkaline phosphate (about three times as much as is required to afford the compound).

Ign.—If heated up too rapidly some loss may be experienced. In contact with C, a partial reduction to metal and consequent loss may occur. The precipitate should be carefully separated from the filter-paper and the same burned separately, or it may be dissolved by means of dilute nitric acid into a weighed capsule and the solution evaporated and finally ignited.

After ignition the precipitate is usually opaque, white, somewhat sintered together; sometimes, without apparent reason, it fuses to a glass.

$ZnS \cdot H_2O$.

Rem.—Usual precipitant, H_2S in neutral solution, or one acid with some organic acid (acetic, citric, formic, &c.). Precipitation can be effected (though slowly) in H_2SO_4 solution; the smaller the proportion of free H_2SO_4 , the more complete the separation. NH_4Cl favours its separation in a granular form, and checks a tendency to run through the filter-paper, which it sometimes exhibits, especially when the solution contains free ammonia. Oxidises slowly on exposure to the air.

Cond.—Solution should be alkaline or acid only with some of the weaker organic acids. Free mineral acids prevent the precipitation to a greater or less extent.

* From School of Mines Quarterly, xii., No. 4.

H_2SO_4 has the least effect, HCl the greatest. Boiling facilitates the formation of the precipitate, but increases the solvent power of acids upon it. Fe should be absent.

Sol.—Dissolved by dilute HCl and HNO_3 or by moderately strong H_2SO_4 when not. Insoluble in alkalies, neutral solutions, and in organic acids, though the latter when in excess retard somewhat its formation. Free ammonia has a similar effect.

Contam.— MnS or NiCO and Fe sulphides. Fe should be separated previously. From the others it may be freed by re-solution, neutralising, and re-precipitating.



Rem.— Na_2CO_3 usual precipitant. When precipitated cold, white and flocculent—by boiling becomes granular and assumes a light brownish shade, probably from oxidation.

Cond.—Solution should not contain bicarbonates or ammonia salts. If CO_2 is evolved by the addition of the precipitant to an acid solution, it must be boiled out. Solution must be rendered alkaline by the reagent.

Sol.—Dissolved by dilute acids, bicarbonates, ammonia salts, and solutions containing citrates, tartrates, sugar, &c. Also by solutions containing large amounts of fixed alkaline salts.

Contum.—Alkaline carbonate requiring several washings (by decantation) with boiling water to remove it. Fe_2O_3 —removed by repeated solution in HCl and re-precipitation with ammonia after igniting the precipitate.

SiO_2 by dissolving the ignited precipitate in acid and filtering off.

Ign.—In contact with air gives black Mn_3O_4 non-volatile. Recent investigations tend to show that the composition is not absolutely constant. If alkali has not been washed out, ignition in contact with the air affords alkaline manganate.



Rem.—Usual precipitant, $\text{NaNH}_4\text{HPO}_4$ or Na_2HPO_4 in presence of ammonium salts. Best managed by adding the reagent to the acid solution of Mn , boiling, and then adding ammonia little by little to the boiling solution, until a slight excess is present, then heating on the water-bath until the precipitate assumes completely the crystalline form.

Cond.—The Mn must be entirely in manganous form, and solution alkaline, though not strongly so. An excess of phosphate (about three times as much as is required to form the combination) must be present. Oxalates must be absent, as well as excessive amounts of ammonia salts or free ammonia.

Sol.—Dissolved by acids. Somewhat soluble in decided excess of ammonia, in NH_4Cl , and some other ammonium salts. The solubility in these last is neutralised by the presence of an excess of the precipitant. When too large proportion of ammonia is present, the precipitate, which should be white or faintly pinkish, becomes deeper in colour, sometimes quite brown.

Contam.—Practically none if bases forming insoluble phosphates are absent and moderate care is used in washing.

Ign.—Converted to $\text{Mn}_2\text{P}_2\text{O}_7$. The temperature should not be too rapidly raised or there may be some loss. The peculiar nacreous lustre of the precipitate is more pronounced after ignition. Sinters somewhat. Not volatile.

(To be continued).

Royal Institution.—The Christmas Lectures to juveniles will this year be on "Life in Motion; or, the Animal Machine" (experimentally illustrated), and will be delivered by Professor John G. McKendrick, M.D., F.R.S., Professor of Physiology in the University of Glasgow.

ELIZABETH THOMPSON SCIENCE FUND.

THIS fund, which has been established by Mrs. Elizabeth Thompson, of Stamford, Connecticut, "for the advancement and prosecution of scientific research in its broadest sense," now amounts to \$26,000. As accumulated income will be available December next, the trustees desire to receive applications for appropriations in aid of scientific work. This endowment is not for the benefit of any one department of science, but it is the intention of the trustees to give the preference to those investigations which cannot otherwise be provided for, which have for their object the advancement of human knowledge or the benefit of mankind in general, rather than to researches directed towards the solution of questions of merely local importance.

Applications for assistance from this fund, in order to receive consideration, *must be accompanied by full information*, especially in regard to the following points:—

1. Precise amount required. Applicants are reminded that one dollar (\$1.00 or \$1) is approximately equivalent to four English shillings, four German marks, five French francs, or five Italian lire.

2. Exact nature of the investigation proposed.

3. Conditions under which the research is to be prosecuted.

4. Manner in which the appropriation asked for is to be expended.

All applications should reach, before December 10, 1891, the secretary of the Board of Trustees, Dr. C. S. Minot, Harvard Medical School, Boston, Mass., U.S.A.

It is intended to make new grants at the end of 1891.

The trustees are disinclined, for the present, to make any grant exceeding three hundred dollars; decided preference will be given to applications for smaller amounts.

(Signed) HENRY P. BOWDITCH, President.
WILLIAM MINOT, JUNR., Treasurer.
EDWARD C. PICKERING.
FRANCIS A. WALKER.
CHARLES SEDGWICK MINOT, Secretary.

October, 1891.

NOTICES OF BOOKS.

Arithmetical Physics. Part II., A. *Magnetism and Electricity* (Elementary and Advanced Stages). By C. W. WOODWARD, B.Sc., Principal (Chemistry and Physics Department) Municipal Technical School, Birmingham. Third Edition. Containing several New Lessons entitled "Qualitative Exercises on Lines of Force." London: Simpkin, Marshall, Hamilton, Kent, and Co. Birmingham: Cornish Bros.

COMPILATIONS of the type of the work before us seem to find no inconsiderable amount of favour. The cause of this is not far to seek. They lend themselves easily to the Anglo-Chinese system of education, i.e., preparing for and passing "exams." Nor do we in the least deny that if kept in strict subordination to intelligent laboratory work they may be exceedingly useful. But we fear that in some institutions the student is trained to solve arithmetical conundrums on physical or chemical questions rather than to do real work. It is well known that for a time the introduction of the physical and natural sciences in college and school curricula met with scant sympathy among official educationalists, on the ground that such subjects did not readily lend themselves to examination purposes. Mr. Woodward's works, and others of a similar tendency, have smoothed over a part of this difficulty.

Our author is of opinion that "some critics feel alarmed when a book has examination questions in it." Our feeling is not alarm, but regret—regret, not so much at

the publication of such questions, as at the system which gives them any value. Every "coach" has on hand collections of former examination papers, and can calculate, with a very fair degree of accuracy, what questions are likely to be put by any given examiner.

The "conscientious teacher"—if he is suffered to exist—aims at training his students to observe accurately and completely, and to draw right conclusions from the phenomena observed. We have had the pleasure of noticing elementary works which proceed on this principle.

CORRESPONDENCE.

CHEMICAL ANALYSIS AND THE PURITY OF WATER.

To the Editor of the Chemical News.

SIR,—In the *British Medical Journal* of October 24th, under the heading "Chemical Analysis and the Purity of Water," there appears an answer to a correspondent—"Medicus"—who had forwarded what purported to be an "analysis" of some water, together with an enquiry as to whether the water referred to was "likely to cause typhoid fever." The heading of this answer as well as the wording of a part of it may be wrongly interpreted.

It is stated—and quite correctly so—that "in the present state of knowledge no chemical analysis would justify the assertion that a water was likely to cause a particular disease." This statement might be taken to imply that some other form of analysis—bacteriological or microscopical, for example—might justify such an assertion; and there exists quite enough misconception about processes for the sanitary examination of water, and more especially about the capabilities of bacteriological examination, to make it highly desirable that the statement should not be understood in the sense indicated above.

As a matter of fact, no process of examination whatever which is capable of practical application for sanitary purposes, will, in the present state of knowledge, warrant the assertion that a water would produce, or would be likely to produce, a particular disease such as typhoid fever. Some over-enthusiastic bacteriologists certainly committed themselves, prematurely, to a contention very like this, and appeared to imagine that waters would be "condemned" or "passed" according to the positive or negative results of cultivation processes applied for the purpose of isolating and recognising specific pathogenic micro-organisms.

Assuming even the possibility of obtaining absolutely positive indications when operating under the necessarily restricted conditions appertaining to sanitary work; by the very nature of the processes of elimination necessary, such results could only be attained with waters which in all probability would already have been condemned by ordinary chemical and microscopical examinations of a tolerably coarse description. But, what is more important, the person who was bold enough to assert the safety of a water upon negative bacteriological results would be an enthusiast of the most dangerous character. Indeed, as was pointed out by Dr. Whitelegge and myself, in 1884 (*Transactions of the Society of Medical Officers of Health*), bacteriological processes in water analysis merely afford an additional test, of a very uncertain kind, for organic pollution. Nothing of a practical nature has been introduced since to justify any stronger assertion. It is noteworthy, by the way, that the counting of micro-organisms (which, when carefully applied, is interesting, if not very valuable) in some hands, even those of "eminent" persons, yields results which are wholly ludicrous.

These notions about the bacteriological "testing" of water have to some extent been fostered by a clumsy

attempt which was made some years ago to depreciate the value, for sanitary purposes, of the chemical analysis of water—an attempt mainly based upon what one of its authors was pleased to term "experiments," but which really consisted of a series of extraordinary ceremonies performed with typhoid stools, London tap water, and Winchester quart bottles. The fallacies underlying this so-called investigation have long since been pointed out, and the statements resting upon it shattered; but the trail of the thing is to be found sometimes, and has, in my opinion, shown itself in the present case.—I am, &c.,

CHARLES E. CASSAL.

Mount Street, W., October 28, 1891.

SAPONIFICATION OF BUTTER.

To the Editor of the Chemical News.

SIR,—I am sorry to learn that Mr. Wanklyn is not satisfied with my last letter. Having myself a perfect knowledge of the circumstances, I have perhaps failed to realise that Mr. Wanklyn is not in the same position.

When I made the statement that Messrs. Wanklyn and Fox had never published a single original experiment, in support of their assertion that the proportion of glycerin yielded by saponification of butter and other fats exhibited no grave departure from the amount required by the accepted view of their constitution, I had in mind the entire absence of original experimental evidence of the kind from the papers read by Messrs. Wanklyn and Fox, in 1883, before the British Association and the Society of Public Analysts. My statement also had reference to the well-known fact that Mr. Fox had made determinations of the proportion of glycerin by a process suggested by Mr. Wanklyn, and that the results of these experiments—for a reason which can only be conjectured—had never seen the light. I had not in my mind the comparatively recently published account of Mr. Wanklyn's solitary experiment, or I should certainly have mentioned it.

On June 6th, at my invitation, Mr. Wanklyn attended a meeting of the Society of Public Analysts, when I read a paper on Saponification, and made in his presence exactly the statement to which he now takes exception. I am sorry he did not, either in the discussion on that paper or in the friendly conversation which occurred between us subsequently, remind me of the omission. I will take care that any prejudice Mr. Wanklyn may have suffered by the omission to mention his experiment shall be remedied at an early date.

With regard to the Chemical Section of the British Association, Mr. Wanklyn need be under no alarm. Only a brief abstract was given at the meeting, as the paper was one of the last on the list for the last day on which the Section met. Mr. Wanklyn well knows what this implies. Hence, on that occasion, I did not actually make the statement to which he takes exception as calculated to mislead, and therefore, as a fact, the Section were not misled by it. The incomplete statement in my paper, as published in these columns, has been duly called to account and corrected by Mr. Wanklyn in this correspondence. I trust this explanation will fully satisfy him, as I am anxious to do him the fullest justice and to avoid any personal friction.

So much for the personal side of the question. The scientific aspect of Mr. Wanklyn's experiment I propose to discuss at an early date. As I have already stated, the published description contains abundant internal evidence of its inconclusive nature.—I am, &c.,

ALFRED H. ALLEN.

Sheffield, Nov. 7, 1891.

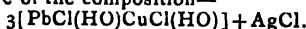
Action of Benzoic Acid upon Oil of Turpentine.
—G. Bouchardat and J. Lafont.—The action of benzoic acid upon turpentines at 150° affords a practical means of reproducing the camphenols and iso-camphenols.—C. R.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 17, October 26, 1891.

On a New Mineral Species, Boleite.—M. Mallard and E. Cumenge.—The mineral in question is obtained near Santa Maria in Lower California. It is a copper and silver ore of the composition—



It is found in cubic crystals of a fine indigo blue, accompanied by anglesite, phosgenite, cerusite, and atacamite.

On Bromostannates.—M. Leteur.—The bromostannates of the alkaline metals and of magnesium are yellow and well-crystallised. The anhydrous bromostannates, those of potassium and ammonium, remain unchanged except in very damp air, but the others are very deliquescent. Their concentrated solutions may be heated without decomposition, but if diluted they become turbid and deposit stannic hydroxide with formation of hydrobromic acid. Alcohol decomposes them slowly in the cold, more rapidly in heat. Benzene has no action upon them. The general method for the preparation of these compounds is to mix the concentrated solutions of the two bromides and to evaporate the mixture in a vacuum or in dry air. The author has obtained and described the salts of ammonium, sodium, lithium, and magnesium.

New Crystalline Ferric Oxychlorides.—G. Rousseau.—The highly concentrated solutions of ferric chloride, containing more than 80 per cent Fe_2Cl_6 , if kept for some time at temperatures between 160° and 220° , give rise to a crystalline ferric oxychloride, $2\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2\text{Cl}_6 \cdot 3\text{H}_2\text{O}$. This compound, on prolonged contact with boiling water, is converted into ferric hydrate ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), completely isomorphous with the original oxychloride. The author has studied the decomposition of solutions of ferric chloride at temperatures above 220° . In the interval between 225° and 280° there were obtained lamellæ of a brownish red, much more bulky than those of the hydrate above described, agreeing in composition with those of the anhydrous oxychloride, $2\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2\text{Cl}_6$. Between 300° and 340° there appear large laminae of a brownish black, $3\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2\text{Cl}_6$, a new oxychloride. It is probable that at temperatures above 350° we should obtain a series of new oxychlorides of the type $(\text{Fe}_2\text{O}_3)^n \cdot \text{Fe}_2\text{Cl}_6$, in which the proportion of Fe_2O_3 would increase regularly with the heat.

Determination of Thallium.—H. Baubigny.—(See page 239).

Solution of Bismuth Chloride in Saturated Solutions of Sodium Chloride, and on Basic Bismuth Salicylate.—H. Causse.—Sodium chloride, like sal-ammoniac, opposes the dissociating action of water upon the salts of bismuth, and by substituting itself for the free acid contained in bismuth solutions it permits the complete neutralisation of the acid, which may be completely converted into bismuth chloride. The author applies his researches to the preparation of basic bismuth silicylate.

Formation of Quaternary Ammonium Iodides by the Action of Trimethylamine in a Concentrated Aqueous Solution upon the Hydriodic Ethers of Certain Primary Alcohols and of a Secondary Alcohol.—H. and A. Malbot.—There are three different modes of reaction between amines and ethers. There is *progression* when a new alcoholic radicle is fixed upon the nitrogen; the ether then simply unites with the amine. There is *stagnation* when the nitrogen simply preserves the radicles already fixed; the ether and the amine unite, with elimination of the diatomic carbide

which enters into the ether. In this manner the amine is reproduced in the state of a salt, which may be characterised as simple reproduction. There is *retrogression* when the nitrogen loses one of its radicles originally fixed; the ether and the amine unite, each losing a mol. of its fundamental carbide. From the totality of the experiments described it appears that whenever the affinity of an amine for an ether is sufficient there ensues a simple union of the two. If this combination takes place integrally in the cold it also takes place integrally in heat. If therefore with certain systems (very numerous) of ethers and amines there is not simple union, but union with elimination of carbides, this elimination is not due to the decomposing action of heat upon the ether, but to a reaction of a new order which is set up between the ether and the amine, and which corresponds to a greater development of energy.

A Characteristic Difference between Substituted Alcoholic Radicles connected respectively with Carbon and Nitrogen.—C. Matignon.—The author arrives at the law that the substitution of an alcohol radicle linked to nitrogen increases the heat of combustion more than the substitution of the same radicle if linked to carbon.

New Albumenoid Substance in the Serum of Human Blood.—C. Chabré.—The author finds in serum a principle distinct from paraglobuline and serine. This compound is present in the blood both of healthy and diseased persons. The author proposes to call it albumone.

Journal für Praktische Chemie.
New Series, Vol. xliii., No. 11.

Action of Hypochlorous Acid upon Monobromquinolines: Bromcarbostyryle and Dibromquinoline.—Ad. Welter.—The author describes the preparation and properties of parabromcarbostyryl, and para-dibromquinoline, of meta-bromcarbostyryl, of meta-a-dibromquinoline, ana-bromcarbostyryle, and ana-a-dibromquinoline.

Researches from the Laboratory of the University of Freiburg.—These comprise a paper by Ad. Claus, and H. Howitz on the halogen alkylates of para-oxyquinoline and the quaternary ammonium hydroxides derived from them by the action of alkalies; and a memoir by Ad. Claus on the mixed fatty aromatic ketones and their oxidation by potassium permanganate.

Calorimetric Researches by F. Stohmann.—The 24th treatise by the authors on the hydration of closed rings.

Revue Universelle des Mines et de la Metallurgie.
Series 5, Vol. xv., No. 1.

Certain recent Discoveries in the Great Chemical Industries.—H. Martin.—The author summarises the present condition of the alkali manufacture. He admits that the Solvay process does not admit of the industrial production of chlorine or hydrochloric acid. The Deacon chlorine process he considers has had its hour of celebrity, but is now abandoned. The utilisation of HCl is now threatened by the attempts to obtain chlorine from the magnesium chloride thrown off as a waste product at Stassfurt. On the Chance process for the recovery of sulphur from vat-waste he pronounces no decided opinion. On the use of gaseous fuel the author quotes a recent memoir by Prof. Lunge.

MEETINGS FOR THE WEEK.

WEDNESDAY, 18th.—Society of Arts, 8. Opening Address of the 138th Session by Sir Richard Webster, M.P.
THURSDAY, 19th.—Chemical, 8. "On Colour Photography," by Capt. W. de W. Abney, F.R.S.
FRIDAY, 20th.—Physical. "A New Theory concerning the Constitution of Matter," by Dr. C. V. Burton.

THE CHEMICAL NEWS.

VOL. LXIV., No. 1669.

CHESTNUT-WOOD TANNIN.*

By Prof. HENRY TRIMBLE.

THE *Castanea vesca* of Linnæus or *C. Sativa* of Miller, variety *Americana*, is a large tree of rapid growth found in many parts of the United States, especially in the eastern section, from Maine to Delaware, and on mountains as far south as northern Alabama.

An extract of the wood and bark has been prepared in this country and France for a number of years. This extract is especially useful in tanning, where it corrects the reddish colour of hemlock, and in dyeing, where it gives a dead black with salts of iron. It must not be confounded with the extract of chestnut oak, *Quercus prinus*, Linnæus, which is also largely manufactured in this country, and, no doubt, the manufacturers are not very particular to keep the two separate.

Most of the literature on the subject of chestnut tannin refers to that from the horse chestnut, *Esculus Hippocastanum*.

In order to leave no room for doubt about the origin of the tannin described in this paper, the chips, free from bark, were collected from a large tree about forty years' old, cut in the month of August.

A summary of the constituents of the wood, as found by a proximate analysis, may be of interest before commencing a description of the tannin:—

	Per Cent.
Crystalline wax, melting at 50° C., soluble in hot 95 p.c. and in absolute alcohol ..	1.03
Gallic acid	0.05
Resin	0.28
Tannin, extracted by absolute alcohol ..	3.42
Mucilage	1.15
Dextrin	1.89
Sugar	0.96
Tannin, extracted by water	1.92
Pectin and albuminoids	1.46
Extractive, dissolved by dilute acid ..	2.95
Ash	7.08
Moisture	7.05
Cellulose and lignin	70.76
	100.00

It is not certain that the gallic acid pre-existed in the wood, because it may have been formed during the drying of the chips, since the analysis was not made for some time after they were cut and ground.

A special determination of tannin on a separate portion of the wood by gelatin and alum and by permanganate and hide powder gave, respectively, 7.86 and 7.85 per cent.

The tannin used in the following experiments was prepared by percolating 24 kilos. of the finely powdered wood with a commercial ether, which consisted of about 74 parts ether, 26 parts alcohol, and a small quantity of water. The ether was recovered from the percolate by distillation and the residue dissolved in cold water. The filtered aqueous solution was precipitated in three portions by lead oxyacetate, the precipitates decomposed by hydrogen sulphide, the latter removed by distillation under reduced pressure, and the solution after cooling agitated with ether, which extracted gallic acid from each of the three fractions. The tannin solution from the middle

fraction was warmed to remove ether and then saturated with common salt. An abundant separation of tannin took place, which was collected, washed with a saturated solution of salt, and dried over sulphuric acid in a vacuum.

The dry residue was dissolved in ether-alcohol, filtered and rapidly evaporated to dryness under diminished pressure, which left the tannin in a porous, light red mass. This was used for some of the qualitative tests, but for many of the reactions the tannin was further purified by again precipitating in three fractions with lead oxyacetate, the lead removed by hydrogen sulphide, the latter removed by distillation under reduced pressure until the liquid had reached a small bulk, when it was agitated with ether, which removed gallic acid from each of the three fractions. The aqueous solution was then distilled to dryness under reduced pressure, the residue in each case dissolved in ether-alcohol, filtered, and rapidly distilled under the same circumstances to dryness, which left the tannin in a nearly white porous mass completely soluble in cold water.

In physical and chemical properties this chestnut-wood tannin so closely resembled gallotannic acid that the following comparative statement is given, to show both the character and resemblance at once:—

Reagent.	Chestnut-wood tannin.	Gallotannic acid.
Ferrous salts.	No change.	No change.
Ferrous chloride and Ammonium hydr.	Blue-black ppt.	Blue-black ppt.
Tartar emetic and Ammonium chloride.	Purple ppt.	Purple ppt.
	Slight clouding.	Slight clouding.
Copper sulphate and Ammonium hydr.	Pale ppt.	Pale ppt.
	No ppt.	No ppt.
Bromine water.	Light brown ppt.	Light brown ppt.
	No ppt.	No ppt.
Calcium hydrate.	White ppt. turning light blue.	White ppt. turning light blue.
Ammonium molybdate.	Yellow colour.	Yellow colour.
Sodium sulphide.	No change.	No change.
Conc. sulphuric acid.	Light yellow.	Light yellow.
Sulphuric acid (1-9).	No deposit.	No deposit.
Lead nitrate.	White ppt.	White ppt.
Cobalt acetate.	Flesh-colored ppt.	Flesh-colored ppt.
Manganese acetate.	White ppt.	White ppt.
Uranium acetate.	Crimson colour, turning dark red.	Crimson colour, turning dark red.
Ammonium picrate.	No ppt.	No ppt.
Potassium bichromate.	Brown ppt.	Brown ppt.
Ferric acetate.	Blue-black colour and ppt.	Blue-black colour and ppt.
Alkaloids.	White ppt.	White ppt.
Gelatin.	White ppt.	White ppt.
Lead acetate.	Light ppt.	Light ppt.

One per cent solutions of the tannins were used as recommended by Procter ("Text Book of Tanning," p. 112), and all the reagents were applied in solution except sodium sulphide. These reactions do not all agree with those given by Procter, but he used a solution of commercial extract of chestnut which may have consisted in part or entirely of chestnut oak, or the difference may be due to the non-tannin constituents of the extract.

The chestnut-wood tannin was found to decompose, when heated to 200° C., into pyrogallol and metagallic acids, an abundant crop of crystals being obtained of the

* Read at the Chemical Section of the Franklin Institute, June 16, 1891.

former. Each of the three fractions was estimated for sugar, and the first found to contain 10.48, the second 7.98, and the third 6.18 per cent of glucose, which no doubt had existed as a glucoside.

The second fraction was dried at 120° C. and submitted to elementary analysis as follows:—

Substance.	
(1) 0.1179 grm.	gave 0.2211 CO ₂ and 0.0486 H ₂ O.
(2) 0.0843 "	" 0.1575 CO ₂ and 0.0363 H ₂ O.

	I.	II.
C	51.15	50.95
H	4.58	4.79
O	44.27	44.26
	100.00	100.00

On calculating for the presence of 7.98 per cent glucose and deducing the difference from (1) we get:—

	Found.	Calculated for C ₁₂ H ₁₀ O ₆ .
C	52.11	52.17
H	4.40	3.10
O	43.49	44.73
	100.00	100.00

It will be noticed that the percentage of hydrogen is greater than that in digallic acid, but in view of the fact that it was dried at 120° C. instead of 140° C., as recommended by Löwe (*Zeit. für Anal. Chemie*, vol. xi., 378), and that it agrees so closely with gallotannic acid in all its reactions, we cannot but conclude that it is gallotannic acid.

An acetyl derivative was prepared which in many respects resembled pentacetyl tannin, but the figures proving it could not be obtained in time for this paper.

A METHOD OF STANDARDISING IODINE SOLUTION FOR THE DETERMINATION OF SULPHUR IN STEEL AND PIG-IRON.

By J. M. WILSON.

I DESIRE to call attention to a method of standardising iodine solution, for use in titrating sulphur in iron and steel, which has been in use in the laboratories of some of the iron works of the Ohio Valley for the past four years, and which, I believe, I was the first to use, in the laboratory of the Laughlin and Junction Steel Co., at Mingo Junction, Ohio.

Finding the hyposulphite method would occasionally fail and frequently gave non-concordant results, on doubling quantities, I cast about for a substitute, and at length settled on a steel the sulphur contents of which had been very carefully determined by all the known evolution methods as a standard.

By using this standard steel I standardised my iodine solution by the same process that I used to determine the unknown percentage of sulphur in the samples of pig-metal and steel submitted for analysis, avoiding the objections raised by certain chemists, that the hydrocarbons evolved with the hydrogen sulphide interfered with the titration by iodine when KOH was used as an absorbent; for the iodine solution being standardised under conditions of actual working, it is to be presumed that, inasmuch as all the C in our standard steel is combined, there will be as much hydrocarbon evolved therefrom as from any sample we may have submitted to us for determination.

As to accuracy, there can be no question on that score, the only essential being that we make sure of complete solution of the metal under treatment by taking plenty of

time to complete the solution of the difficultly soluble sulphides, &c., which invariably accompany high sulphur irons, and making sure of absorbing all the evolved H₂S.

It is sufficiently rapid to suit the most fastidious, as it requires no more time than is required to make the sulphur determination in the ordinary routine of laboratory work.

Below I add a few comparative results obtained in the course of work about a busy steel plant laboratory, and which are not picked, nor were they made for the purpose of establishing the method of standardising, as that had been in use almost four years before these results were obtained, but were made for the purpose of convincing the president of a certain furnace company that our method of sulphur determination was accurate and comparable with that used by his chemist.

The determinations by the iodine method were made by my assistants, those by Br and HCl by myself.

	By Iodine.	By Br and HCl.
Car 2238.	0.067 p. cent S.	0.063 p. cent S.
" 2238. 2nd sample.	0.060 " "	0.064 " "
" 3614.	0.069 " "	0.072 " "
" 4326.	0.080 " "	0.071 " "
" 4326. 2nd sample.	0.069 " "	0.075 " "
" 8113.	0.073 " "	0.063 " "
		0.068 " "
		0.068 " "

The above are all the comparative determinations made at that time, October and November, 1890.—*Journal of Analytical and Applied Chemistry*, August, 1891.

ELECTROLYTIC DETERMINATION OF METALS AS AMALGAMS.*

By G. VORTMANN.

(Concluded from p. 242.)

Separation of Lead in Alkaline Solutions.

LEAD may be also quantitatively eliminated as an amalgam from an alkaline solution. The salt of lead is dissolved in water along with mercuric chloride, a few grms. of tartaric acid are added and then an excess of soda-lye. There is produced a brown precipitate which readily dissolves on the addition of potassium iodide. The liquid is diluted with water as far as the size of the capsule permits, and the electric current is passed through. The lead is entirely separated out as an amalgam without the formation of peroxide. The electrolysis is completed as soon as a sample of the liquid shows a pure white turbidity on the addition of ammonium sulphide.

The amalgam must be washed with water only, as alcohol occasions loss. In order to dry the amalgam as rapidly as possible it is washed several times with hot water, allowed to drain, and dried in a current of air; as it is quickly oxidised whilst moist, the results obtained are in general too high, so that this process may be recommended for the separation of lead from other metals (tin and arsenic), but not for determination.

For the separation of lead from other metals (tin, antimony, arsenic) its precipitation from an ammoniacal solution will be very suitable, though a part appears as peroxide. I mixed the solution of lead nitrate and mercuric chloride with tartaric acid, then with ammonia in excess, and conducted the electric current through the liquid until a specimen remained clear on the addition of ammonium sulphide. The lead was chiefly deposited as amalgam, but a small quantity appeared as peroxide at the positive electrode; I decanted off the liquid, washed both electrodes with water, put in the platinum capsule a solution of sodium acetate, acidified with acetic acid and

* *Berichte Deutsch. Chem. Gesell.*

mixed with sodium nitrite, and passed the current through until lead could no longer be detected in the liquid. The ammonia was then washed and dried as recommended above.

On the electrolysis of the ammoniacal solution the lead amalgam was partly deposited in a spongy form, though strongly adherent. On the electrolysis of the acetic solution the spongy mass gradually disappeared entirely, and the amalgam finally formed a uniform mirror-like surface. This experiment showed plainly that in order to obtain a uniform amalgam on the electrolysis of ammoniacal solution the quantity of mercury present must be greater than on employing an acid solution. The same fact was observed in the case of zinc and bismuth.

Determination of Bismuth.

The separation of bismuth as an amalgam is best effected by means of acid solutions. The double ammonium oxalate is not well suited for its determination, because bismuth oxalate is much too sparingly soluble in the solution of ammonium oxalate. In order to prevent the precipitation of basic salts there must always be present a moderate excess of free acid, which again must be avoided from various reasons; for in presence of much free nitric acid there is formed at the positive electrode a larger quantity of bismuth peroxide, and the complete separation of the metals is effected less easily. They must, if possible, be washed without interrupting the current. In presence of much free hydrochloric acid there ensues at the positive electrode a strong development of hypochlorous acid, which is very annoying to the operator. I avoided the use of a large excess of hydrochloric acid by the addition of potassium iodide, when the bismuth iodide, which is deposited at first, re-dissolves in the excess of potassium iodide to an orange-yellow clear liquid, which may be diluted with water without any deposition of basic salts. A second method of avoiding too large an excess of free acid (in case of hydrochloric solutions) consists in diluting the liquid not with water but with ethylic alcohol, since both mercuric chloride and bismuth chloride are readily soluble in alcohol, and the solution remains perfectly clear even on addition of a large quantity of alcohol.

For the confirmatory analyses there was used pure bismuth oxide (calculated as 89.69 per cent bismuth), which I obtained partly by igniting basic bismuth nitrate, partly by oxidising metallic bismuth with nitric acid. Professor Dr. A. Classen kindly placed at my disposal the purest metallic bismuth which he has obtained for the determination of its atomic weight, for which I here express my best thanks.

1. *Separation of Bismuth from a Solution of Potassium Iodide.*—Bismuth oxide, along with a weighed quantity of mercuric chloride, was dissolved in hydrochloric acid in the platinum capsule; solution of potassium iodide was then added until the precipitate formed at first was re-dissolved, and the liquid was diluted as far as possible with water. On the electrolysis of this liquid the bismuth amalgam separated out very well, whilst the free iodine collected on the surface in the form of a mass filled with bubbles. When a sample of the liquid remained perfectly clear after the addition of ammonia and ammonium sulphide, I poured, without interrupting the current, a few c.c. of concentrated soda-lye into the capsule until the iodine was entirely dissolved, and continued passing the reinforced electric current for an hour until a sample of the liquid, after the addition of sodium sulphite (in order to reduce the iodate) and ammonium sulphide, no longer gave a brown colouration. The amalgam was then washed and dried in the ordinary manner.

Bismuth amalgam, if sufficient mercury was used, is of silvery metallic lustre; if the quantity of mercury was too small it is covered with a blackish brown layer of amorphous bismuth, which adheres so firmly that nothing is lost on cautious rinsing. The amalgam is stable in the air; the weight does not vary after several days'

preservation in the exsiccator or even in the open air. If heated for three hours in the air-bath at 90° neither its weight nor its appearance is altered.

2. *Separation of Bismuth from a Hydrochloric Solution mixed with Alcohol.*—The mixture of bismuth oxide and mercuric chloride was dissolved in hydrochloric acid; the solution was mixed with about 50 c.c. of alcohol at 96 per cent, mixed by stirring with the positive electrode, and water was gradually added, with constant stirring, until the surface of the liquid was at least 1 c.m. below the margin of the capsule, when the electric current was introduced. It is not advantageous to dilute the solution of the chlorides exclusively with alcohol, since an alcoholic solution is much disposed to creep over the edge of the capsule, thus occasioning loss. If we use a mixture of alcohol with two volumes of water, creeping does not occur. The bismuth amalgam is uniformly deposited as a mirror-like surface, whilst acet-aldehyd and its chlorine substitution products are formed at the positive electrode. As soon as a sample of the liquid remains clear on the addition of ammonia and ammonium sulphide the liquid is decanted off, and the amalgam is quickly washed in the usual manner. In some cases the author has neutralised the free acid by an addition of soda-lye before decanting off the liquid.

Both the above methods give good results, whether the bismuth is present in a small or a large quantity. In presence of much bismuth, however, the second method is preferable, as according to the former method a large quantity of potassium iodide would be required for the formation of the double salts, which involves the separation of an unpleasantly large quantity of iodine in electrolysis.

3. *Separation of Bismuth from Nitric and Ammoniacal Solutions.*—Bismuth may also be separated as an amalgam from a nitric solution, but the relative proportion of mercury must be much larger (to 1 part of bismuth at least 4 parts of mercury). The formation of bismuth peroxide is avoided by the addition of tartaric acid. I dissolved bismuth and mercuric oxide in nitric acid, added tartaric acid, and diluted with water. The amalgam obtained on electrolysis was washed and dried in the usual manner. The mercuric oxide contained 92.076 per cent of mercury.

From an ammoniacal solution mixed with tartaric acid bismuth may likewise be completely deposited as an amalgam; but here, as in the case of a nitric solution, much mercuric chloride must be used, as the bismuth is otherwise in part deposited in the form of an amorphous blackish brown powder which can scarcely be washed in water without loss. I should therefore not recommend the separation of bismuth as an amalgam from an ammoniacal solution for its determination, but merely for its separation from other metals (e.g., tin, antimony, and arsenic).

It is well known that the electrolytic determination of antimony presents peculiar difficulties, and that a good adhesive deposit is obtained only by means of careful work, and, according to Prof. Classen, in presence of not more than 0.16 grm. of antimony. The solubility of mercury in solution of sodium sulphide, and the ease with which this metal is precipitated electrolytically, made it *a priori* likely that the determination of antimony as an amalgam would be readily practicable. In fact it presents no difficulties. About 2 parts of mercury must be present in solution to 1 part of antimony; a larger proportion of mercury is not injurious, and it is even advantageous if the quantity of antimony is large. As mercurial salts are reduced by antimony oxide in alkaline and sulph-alkaline solutions with separation of metallic mercury, the antimony must always be present in the form of pentoxide. I dissolved a mixture of tartar emetic and mercuric chloride in hot water, with an addition of strong bromine water, until the solution when completely effected was coloured yellow by free bromine. I then added the solution of sodium sulphide mixed with sodium hydroxide (as

indicated by Prof. Classen) until the precipitate formed at first was re-dissolved. The solution was then diluted with water as much as the size of the platinum capsule allowed, and the electric current was introduced. Here also, as in the determination of mercury alone, a small quantity of black mercury sulphide was deposited at the positive electrode, which disappeared again towards the end of the operation, so that the positive electrode was ultimately coated with a thin layer of yellow sulphur. When a sample of the liquid, on the addition of dilute sulphuric acid, gave a pure white milky precipitate, the liquid was poured off and the amalgam was washed and dried in the ordinary manner.

Antimony amalgam has a steel-grey colour and is permanent in the air; it dissolves completely in a mixture of tartaric acid and dilute nitric acid, generally leaving upon the capsule a very thin stain of platinum black. The separation of antimony has the advantage that large quantities can be separated at pleasure, if only the vessel in which the electrolysis is performed is sufficiently capacious. As tin, when present as oxide, can be electrolytically deposited neither from a concentrated alkaline solution nor from an alkaline sulphide, the amalgam method will probably be very suitable for separating tin from antimony.

If an ammoniacal solution of antimony mixed with tartaric acid is submitted to electrolysis, no antimony is deposited. This non-precipitability of antimony from an ammoniacal solution will probably be very useful for its separation from lead, bismuth, and other metals.

Separation of Arsenic as an Amalgam.

My experiments for the electric determination of arsenic as an amalgam have hitherto proved fruitless. The arsenic escapes entirely, or in part, as arsenic hydride.

The author is continuing his experiments on this method of separating different metals, and reserves to himself its further development.

DETERMINATION OF SMALL QUANTITIES OF ALKALI AND RECOGNITION OF THE NEUTRALITY OF WATER.

By F. MYLIUS AND F. FOERSTER.

(Continued from p. 240).

ALTHOUGH here (perhaps from a trace of iron present in the zinc sulphate) the solubility of the solution seems imperfect, it appears from the experiment that, by means of our process, 0.002 per cent of free zinc oxide or of free sulphuric acid may be detected in crystalline zinc sulphate. In case of zinc salts, methyl orange is generally used as indicator for the detection of free acid. When this colouring-matter was used it was possible to add to a solution of 5 grms. zinc sulphate 100 c.c. N/1000 sulphuric acid without completing the change from the yellow to the red colour.

Solutions of zinc chloride may also be satisfactorily neutralised by means of the eosine reaction, or their percentage of neutral salt may be determined. In an apparently neutral solution of this salt the proportion of Zn:Cl was found 1:2.01.

Whilst in the salts of magnesium, cadmium, manganese, nickel, and cobalt, the reactions are like those of zinc, the oxide salts of iron, aluminium, and chrome behave with eosine like free acids. Lead and silver yield, with iodeosine, salts of a fine violet colour; they are insoluble in water, whereby the use of eosine in testing the salts of these metals is rendered more difficult.

Least iodeosine should appear as a universal indicator, it must be pointed out that it is unsuitable for the determination of organic acids. The determination even of oxalic acid with millenormal alkali gives no quite accu-

rate values; with the weaker acids, such as acetic or formic acid, titration with eosine is impracticable, as there occurs no distinct change of colour.

Colorimetric Determination of Alkali.

Titration with millenormal solutions permits us to determine in 100 c.c. of water quantities of alkali equivalent to 0.1 m.grm. Na₂O. For smaller proportions the method above mentioned may be modified into a colorimetric process. Such determinations, which are much used in other branches of analytical chemistry when the estimation of "traces" comes into question, have hitherto not been employed in alkalimetry. With the aid of iodeosine we may obtain a colorimetric method for alkalimetry on the bases of the following facts:—If a very dilute aqueous solution of alkali is shaken up with an ethereal solution of eosine, the eosine being in excess with reference to the alkali, the solution of the alkali takes a more or less intense rose-colour in proportion to the quantity of alkali present. From the intensity of the rose-colour obtained we may infer the quantity of alkali present in the solution. For this purpose it is necessary to operate in a strictly definite manner. We have to attend to the purity of the water and the eosine to be used, and the proportion of colouring-matter in the ethereal solution, and the volumes of the two liquids which come into contact. All the vessels employed must be of the best quality of glass, lest an error might arise from alkali taken up during the operation.

The conditions to be observed in the colorimetric process follow from the behaviour of iodeosine and its alkaline salts with water and ether.

On the ground of the complete precipitability of the colouring-matter from its alkaline solutions by acids, we are tempted to draw the conclusion that free eosine is insoluble in water, which would explain the slow change of colour on neutralisation from the hydrolytic splitting up of the alkaline salt. But this inference is inadmissible; free eosine is soluble to a slight extent in pure water, with the same rose-colour which appears in a dilute alkaline solution. No difference between the alkaline and the aqueous solutions can be perceived either on examination with the naked eye or on the observation of the absorption spectrum. The red colour remains even when a small quantity of acid is added to the aqueous solution. The colour disappears only on the addition of a large excess of acid, when the colouring-matter is precipitated in orange-yellow flocks.

We have here evidently to do with two modifications of eosine. As the yellow precipitated iodeosine is anhydrous, the assumption is natural that the red soluble modification is a hydrate, which is converted into the yellow anhydride by dehydrating agents, such as acids. This agrees with the circumstance that the yellow solutions of the colouring-matter in alcohol or acetone turn the redder the more water is added to the solution. It is also known that the alkaline solutions when highly concentrated have a yellower tone than when dilute. In support of this view it may be stated that in the fluoresceins the two modifications—the hydrate and the anhydride—may be isolated at pleasure. We must not omit to point out that, even without the above assumption, the facts observed can be satisfactorily explained on the basis of the electrolytic theory of dissociation and its consequences.

The red solution of iodeosine hydrate in water is decolourised by shaking up with a relatively large quantity of ether. Although aqueous ether has a much greater solvent power for the colouring-matter than has water, yet the latter, if shaken up with an ethereal solution of eosine, takes up a little eosine and assumes a red colour. The quantity depends on the proportions of the three active substances, and is constant if the conditions remain unaltered.

The rose-colour of the dissolved alkaline eosinates decreases in intensity proportionally to their dilution. It

is not affected, at least in high solutions, by the presence of an excess of alkali or of neutral salts.

As in a colorimetrical determination the ethereal solution of eosine is in excess with reference to the alkali, there arises the question whether under such conditions we have the formation of neutral or acid salts. Experiment shows that neutral salts only are formed. 0.4014 gm. iodeosine was dissolved in a slight excess of decinormal soda-lye; the solution, with occasional shaking, was mixed with ether and so much decinormal sulphuric acid that the first trace of eosine passed into the ether; a further quantity of acid caused then at once a corresponding quantity of eosine to pass into the ethereal solution. It appeared that the alkali combined with the eosine had been furnished by 9.7 c.c. of decinormal solution, and consequently that the salt $C_{20}H_6Na_2I_4O_6$ had been formed, whilst the acid salt, $C_{20}H_7NaI_4O_5$, would require only half as much. Hence it follows that the acid salt is not permanent in an aqueous solution in presence of ether, but is at once resolved into the neutral salt and free eosine.

The other alkalies behave like soda. Hence, from the quantity of the dissolved eosine, the quantity of the alkali present in the solution and combined with the eosine should follow in the most simple manner. But this is not exactly the case.

We have found that dilute alkaline solutions withdraw rather less colouring-matter from the ethereal solution of eosine than would be required for the formation of the neutral salt. We explain this circumstance by the fact that even the neutral alkaline salts of iodeosine are not perfectly permanent in water, and, in consequence of the slight decomposition caused by the water, they give off a small quantity of free eosine to the ether.

According to our experiments sodium eosate is not taken up by ether.

(To be continued.)

ON THE MUTUAL REACTION OF FERRIC SALTS AND SOLUBLE SULPHO- CYANIDES.

By GERHARD KRÜSS and HERMANN MORAHT.

THE pamphlet before us is a reprint from Liebig's *Annalen der Chemie*.

From the author's researches it appears that on mixing ferric salts with an excess of potassium sulphocyanide there is always formed a double salt containing 9 mols. of potassium sulphocyanide.

If to an excess of ferric salt there is added but little potassium sulphocyanide it is perhaps possible that free ferric sulphocyanide is present in the solution; still this is not probable, as the double compounds of ferric sulphocyanide with the alkaline sulphocyanides are more permanent than the former alone.

If a solution of the iron salt is diluted with distilled water in a beaker until the liquid has only a faint yellow tint, and if a concentrated solution of alkaline sulphocyanide is then added, there appears at once the deep cherry-red colour of the double sulphocyanide of the formula—



ON THE SULPHO-SALTS OF VANADIUM.

By GERHARD KRÜSS and KARL OHNMAIS.

THIS memoir has been reprinted in a separate form from Liebig's *Annalen der Chemie*.

We notice the methods which have been used for the determination of vanadium. The sulpho-salts, on igni-

tion in the air, yield vanadium pentoxide, which can be weighed as such.

The ammonium salt is heated in a covered porcelain crucible until the sulphur and the ammonia are expelled; it is then ignited with excess of air until the weight is constant, which is generally effected in an hour, and may be accelerated by passing oxygen over the fused mass. An addition of ammonium nitrate is not recommended, as loss may be readily occasioned by spitting.

The determination of vanadium in salts with fixed alkalies was first effected by a volumetric method depending on the reduction of the acid solution of a vanadate to vanadium tetroxide by means of sulphurous acid, and subsequent oxidation of the tetroxide to vanadic acid by solution of permanganate. More recently the authors have adopted the method which C. Friedheim has proposed for the separation of tungstic and vanadic acids.

ON THE OCCURRENCE OF NITROGEN IN URANINITE, AND ON THE COMPOSITION OF URANINITE IN GENERAL.*

By W. F. HILLEBRAND.

(Continued from p. 247.)

Analyses of Uraninite.

THE analyses which follow were, with two exceptions, V. and XVIII., made before recognition of the nature or importance as regards quantity of the gas given off by acid, and, as before said, their object was chiefly to ascertain the relative percentages of UO_2 , UO_3 , and rare earths with a reasonable degree of accuracy.

The specific gravities of the Connecticut mineral were so much higher than any published that considerable care was exercised in their verification and in all subsequent determinations. The figures given represent the density of the mineral dried at $100^\circ C.$, for the small amounts of hygroscopic moisture, varying as they did with different specimens, would exert a marked effect on the result if included.

A knowledge of the condition of the iron, which all analyses show accompanies uraninite in small quantity, is of prime importance for the correct volumetric estimation of UO_2 . Comstock and Blomstrand have both assumed that it exists in the ferrous condition, and from the oxygen transferred in titration have deducted a corresponding amount before calculating UO_2 . While not in a position to deny the correctness of this assumption for a portion of the iron at least, I have, with one or two exceptions which will be noted in due order, preferred to consider all iron dissolved by dilute nitric acid as ferric oxide, and for the following reason:—The matter insoluble in dilute nitric acid may consist of columbite, feldspar, quartz, mica, a very sparingly soluble phosphate, and the reddish infiltration matter filling the minute seams in the mineral, substances which it is practically impossible to remove entirely from any sample containing them. When the uraninite is dissolved this insoluble matter is decidedly red (unless columbite predominates largely) from ferric oxide, of which it is probable the infiltration matter is largely composed. In all such cases a large percentage of the insoluble matter is ferric oxide, and only in one case could any ferrous oxide be found in it aside from that belonging to columbite. It was further noticed that more iron was found in solution, and correspondingly less in the insoluble, when the heating had been prolonged beyond the usual time or when a stronger acid was employed. It seemed therefore certain that a portion of the iron in solution had been derived from

* From "Bulletin No. 78, U.S. Geological Survey, 1889—90." An abstract of this paper was published in the *Am. Jour. Sci.*, vol. xl., p. 384.

TABLE I.—Uraninite from Glastonbury, Connecticut.

	I.			II.	III.	IV.	V.		
	a.	b.	Mean.				a.	b.	Mean.
UO ₃	—	—	22'08	23'35	22'22	(e) 26'48	23'13	22'94	23'03
UO ₂	59'09	59'17	59'13	58'01	(c) 59'31	(f) 57'43	—	—	(g) 59'93
ThO ₂	9'09	—	—	9'78	—	9'79	10'01	—	—
CeO ₂	—	—	—	—	—	0'25	0'29	—	—
ZrO ₂ ?	—	9'50	9'57	—	10'31	—	0'15	11'13	11'10
(LaDi) ₂ O ₃	—	—	—	—	—	0'13	0'15	—	—
(YEr) ₂ O ₃	0'55	—	—	0'46	—	0'20	0'48	—	—
PbO	3'14	—	3'14	3'24	3'07	3'26	3'08	3'08	3'08
CaO	0'08	—	0'08	—	undet.	0'08	0'17	0'04	0'11
MgO	—	—	—	—	undet.	—	—	—	—
Alk.	—	—	—	—	undet.	trace	—	—	—
H ₂ O	0'97	—	0'97	undet.	undet.	0'61	0'43	0'42	0'43
N	undet.	undet.	undet.	undet.	undet.	undet.	—	—	(h) 2'41
Fe ₂ O ₃	(a) 1'21	—	1'21	0'33	(d) 0'67	0'40	0'28	0'29	0'29
MnO	—	—	—	—	—	trace	—	—	—
SiO ₂	1'06	—	1'06	—	0'25	0'16	0'15	0'18	0'16
P ₂ O ₅	—	—	—	—	—	—	0'02	—	0'02
Fl	—	—	—	—	—	—	0'04	—	0'04
Insol.	0'85	—	0'85	(b) 1'74	0'42	0'70	0'85	0'92	0'89
Cb ₂ O ₅	0'96	—	0'95	—	—	—	—	—	—
Total	—	—	99'05	96'91	96'25	99'49	—	—	101'49
All U as UO ₂ ..	—	—	79'98	80'06	80'29	82'43	81'75	81'59	81'67
Sp. gr.	—	—	9'139	9'051	—	9'587	—	—	9'622
Temp. °C. .. .	—	—	174	21	—	21	—	—	19'4

(a). Estimated by weight; probably contaminated by earths or by alumina. Another fragment gave 0'43 Fe₂O₃.

(b). Containing 0'55 SiO₂, 0'86 Fe₂O₃, 0'33 Al₂O₃, &c.

(c). Mean of 59'07, 59'15, and 59'71. Separation by HFl gave 60'05.

(d). Too high, since it was estimated by weight and found to contain some rare earths.

(e). Gravimetrically after separation by HFl there was found 28'58 and 26'89.

(f). Mean of 57'46 and 57'39. Probably too low, and UO₃ consequently too high, since they were among the earlier determinations made and no material was left for verification after the method was perfected.

(g). Mean of 59'88, 60'07, and 59'83.

(h). Mean of 2'39 and 2'46 by decomposition with H₂SO₄ in sealed tubes, and 2'33 and 2'46 by fusion with NaKCO₃ in a current of CO₂. The first determinations were made in the apparatus shown (see ante), and gave 2'14 and 2'21 per cent, but decomposition was incomplete and the percentage was calculated on the assumption that the undissolved residue had the same composition as the portion dissolved, a view hardly tenable in the light of subsequent experiments. They are, therefore, not used in deriving the mean given in the analysis.

ferric oxide of the gangue, and possibly all of it. It was impossible to tell how much, if any, might have existed in the ferrous condition, and therefore it seemed better to count the whole as ferric oxide. In any event the amount found is always so small as to affect the percentage of UO₂ but slightly, and never enough to cause trouble in comparing different analyses. That none of the iron belongs to uraninite itself appears from an experiment made upon Glastonbury material (No. V.). When boiled for many hours with dilute hydrochloric acid till 25 per cent of the mineral had dissolved, not a trace of iron was left in the undissolved portion.

Proof is likewise lacking of the state of oxidation of cerium, but CeO₂ seems its more natural condition in the presence of other binoxides in overwhelming proportion. As with iron, however, its small amount renders this for purposes of calculation a matter of small importance.

It must be borne in mind that the combined earths are probably too low in all cases except Nos. V. and XVIII., in which two precipitations of nitrates by ether were made to separate the last traces of earth from uranium. It is assumed that separation is then perfect, for by no known means could a further trace be extracted. That an appreciable amount of earths escaped separation in other analyses, and went to increase the apparent percentage of UO₃, was at one time shown in working up some of the residues, amounting to 10 or 12 grms., for pure U₃O₈,

when a considerable weight of earths was obtained, amounting to at least one-third of 1 per cent of the residues.

I. From a large crystal nearly an inch across, which was collected by Prof. F. W. Clarke, the analysis of which led to all subsequent work. It was much contaminated with reddish felspar, quartz, yellow muscovite, and, as examination of the insoluble showed, with columbite, besides a reddish infiltration product lining cracks and becoming apparent on broken surfaces. Most of these were removed, but enough remained to render the analysis in some respects unsatisfactory. The amount of soluble silica indicated thorite as a possible source of the thorium, which the other analyses show cannot be the case. The presence of such an amount of columbic acid in a readily soluble form—for it was obtained by boiling the nitric acid solution of the mineral after filtration from the insoluble matter—points to some columbate other than columbite. Microscopical examination of a thin section of the crystal showed a few cracks filled with a reddish brown and yellow material, part of which was a readily decomposable silicate of some kind, as evidenced by the fuchsine test after treatment with hydrochloric acid and washing with water, but the total visible impurity was very little. A portion of the water undoubtedly belonged to the foreign matter.

II. Obtained from Prof. W. N. Rice, Middletown, Conn.

TABLE II.—*Uraninite from Branchville, Connecticut.*

	VI.	VII.	VIII.	Comstock's analysis.
UO ₃	13'27	21'54	14'00	40'08
UO ₂	72'25	(a)64'72 (b)70'99	54'51	54'51
ThO ₂	7'20	6'93	6'52	—
ZrO ₂ ?		0'33	—	—
PbO	4'35	4'34	4'35	4'27
MnO	0'10	0'07	?	—
CaO	0'18	0'22	0'30	—
MgO	—	—	0'15	—
Alk.		—	—	—
H ₂ O	0'68	0'67	(c) 0'68	0'88
N	undet.	undet.	(d) 2'63	—
Fe ₂ O ₃	0'11	0'28	0'27	FeO 0'49
SiO ₂	0'03	0'13	0'20	—
Insol.	0'04	0'14	(e) 1'40	—
Total	98'21	99'37	101'49	100'23
All U as UO ₂ ..	84'78	85'06	84'21	—
Sp. gr.	9'733	9'560	9'348	—
Temp. °C	27'7	0'30	15'7	—

(a). No material was left for a verification of this figure after perfection of the method of UO₂ estimation: but the low density compared with that of the others when corrected for insoluble matter of 2'7 sp. gr., and the fact that a UO₂ determination by Zimmerman's method (p. 232), in which, however, decomposition was not quite complete, gave 63'28 per cent, point to its correctness.

(b). Mean of 71'11 and 70'87.

(c). Assumed as in VI.

(d). Only enough material for a single estimation was left, and being one of the earliest made it was carried out in the apparatus depicted on p. 245, wherein only 89'7 per cent of the powder had dissolved after about 210 hours, when the experiment was discontinued because of danger of breakage to the flask. The figure here given is calculated on the basis of like composition for the dissolved and undissolved portions,—an improbable assumption in the light of later experiments,—and is probably too low.

(e). The gangue was mainly reddish felspar, and contained 0'31 (or 22 per cent) Fe₂O₃ besides, but only an indeterminate trace of FeO as ascertained in a separate portion. The increase in the percentages of CaO, alkalis, and SiO₂, with progressive increase of insoluble matter, indicates clearly a partial solution of the felspar.

III. Collected by myself as small crystals and fragments. Only a very small amount was available.

IV. Obtained from Mr. E. F. Sheldon, of Middletown, Connecticut.

V. From the same source as No. IV., but at a later date. A very large irregular crystal of this lot was crushed and purified as far as possible, and with this material a very careful analysis, duplicated in part, was made for the purpose of obtaining an accurate summation. This analysis post-dates all others published in this paper except No. XVIII. In addition several estimations of nitrogen were made by the different ways mentioned already, and numerous experiments which it was hoped might throw light upon the ultimate composition of the mineral.

All the above material came from Hales's quarry, in the town of Glastonbury, a few miles north-east of Middletown, Conn.

VI., VII., VIII.—This material was all received from

Profs. Brush and Dana, of New Haven, and was the residue of the material from which Comstock had taken his for analysis. No. VI. was by far the purest of any material obtained from any locality, the crystals and fragments being brilliant and well defined and almost absolutely free from impurity. It is earnestly to be hoped that more of this excellent material may be found at Branchville for closer investigation, since it represents the extreme of perfection as regards crystallisation and freedom from attached and infiltrated foreign matter, besides possessing the greatest density and the highest percentage in UO₂ and nitrogen of any known variety.

(To be continued).

PROPERTIES OF PRECIPITATES, &c.*

By E. WALLER, Ph.D.

(Continued from p. 248).

MnO₂ (or MnO₂H₂O, MnO₂·2H₂O, &c.).

Rem.—For separation in two separate cases. 1. From acetate solution by addition of an oxidising agent, usually Br. 2. From a boiling solution in nitric acid, by addition of crystals of KClO₃. Also (3) obtained in titration by the Volhard method—adding standard (volumetric) solution of K₂Mn₂O₈ to a solution neutralised by ZnO. In all cases the precipitate probably contains some water of constitution (hydrated oxide).

Cond.—Absence of HCl or other halogen acids, lower oxides of nitrogen or reducing agents. In Case 1, a fair proportion of alkaline acetate must be present, to supply base to the mineral acid which might otherwise be set free. Boiling solution necessary.

Sol.—Dissolved or prevented from forming by dilute mineral acids, particularly HCl. Insoluble in moderately strong acetic or in concentrated nitric. When formed it is soluble in strong HCl, forming temporarily an olive-green solution of Mn₂Cl₆, which becomes practically colourless MnCl₂ by heating. Readily dissolved by HCl or H₂SO₄ in presence of reducing agents (SO₂, H₂C₂O₄, FeSO₄, &c.).

Contam.—Salts of fixed alkalis, Fe₂O₃, ZnO.

Ni (Electrolytic).

Rem.—Requires a stronger current than Cu—two or three Bunsen cells (12 to 14 c.c. oxyhydrogen gas per minute). The rapid deposition of the metal is somewhat checked as soon as a coating of nickel has formed, tending to be slower the thicker the coating. This peculiarity is most marked in cold solutions. In preparing for weighing it is treated as electrolysed Cu, by washing with water, then with alcohol, and drying at a gentle heat.

Cond.—Solution should contain no other metals of the (NH₄)₂S or H₂S groups. Chlorides should be preferably absent. The solution should contain the nickel as double ammonium nitrate, sulphate, or oxalate (the latter most advantageous), and excess of ammonia. The operation is more rapid at 70° C. In consequence, ammonia requires to be added from time to time.

Sol.—Dissolves readily in HNO₃, especially with the aid of heat. Slowly soluble in strong solution of (NH₄)₂C₂O₄.

Contam.—Co, Fe, and Zn, being precipitated from oxalate solution under the same or similar conditions, may be present in the coat unless previously separated.

Ni(OH)₂ and Ni₂(OH)₆.

Rem.—Usual precipitant, KOH or NaOH. If the solution contains free halogens, or hypochlorites, hypobromites, &c., Ni₂(OH)₆ may be precipitated black. The most marked characteristic of the precipitate is the per-

* From School of Mines Quarterly, xlii., No. 4.

sistency with which it takes up and retains impurities derived from the solution.

Cond.—No bases other than fixed alkalis should be present.

Sol.—Dissolved readily by mineral acids. Soluble or prevented from precipitation by NH_4 salts and tartrates, citrates, &c., or other organic solutions.

Contam.—Alkali used as the precipitant, Fe_2O_3 , Al_2O_3 , and silica from the reagents. The precipitate requires thorough washing by decantation with boiling water. After ignition and weighing, it should be dissolved in HCl , which leaves SiO_2 and Al_2O_3 . From this solution the iron should be precipitated by ammonia, filtered, redissolved, and re-precipitated again, and these impurities ignited, weighed, and the weight deducted.

Ign.—If only moderately, some Ni_2O_3 is contained in the precipitate. If strongly ignited, it all becomes green NiO . The tint is not a pure green like that of ignited Cr_2O_3 , but lighter and somewhat muddy.

$\text{NiS.H}_2\text{O}$.

Rem.—For separation only. Usual precipitant H_2S in weak acetic solution, or $(\text{NH}_4)_2\text{S}$ followed by acetic acid in excess. Oxidises easily in contact with the air, with partial formation of NiSO_4 . Should be washed by and kept in contact with H_2S water during manipulation.

Cond.—Absence of other members of $(\text{NH}_4)_2\text{S}$ or H_2S group. NH_4Cl in the solution assists materially its separation in the granular form. Free ammonia, on the other hand, tends to keep the precipitate suspended in the liquid. The solution should be only slightly acid with acetic acid or else barely alkaline.

Sol.—Formation of the precipitate prevented by moderate amounts of free acetic acid or mineral acids. When once formed, it is insoluble in these menstrua unless oxidised by exposure to air, which may easily occur. Somewhat soluble in $(\text{NH}_4)_2\text{S}$. To meet these peculiarities of the compound, the solution should be rendered alkaline with ammonia, and H_2S passed in, or $(\text{NH}_4)_2\text{S}$ added, and when the precipitate is fully formed, the solution is acidified with acetic acid, and the precipitate allowed to settle (which occurs readily if NH_4Cl is present). Soluble in hot HNO_3 or in aqua regia. Soluble in KCy .

Contam.—Sulphides of $(\text{NH}_4)_2\text{S}$ group, if not previously separated.

Ign.—Gives mixture of oxide and sulphate.

$\text{Co}_2(\text{NO}_2)_6.6\text{KNO}_3$.

Rem.—Usual precipitant, KNO_3 in a solution slightly acid with acetic. Yellow crystalline precipitate, forming best in a warm solution.

Cond.—Solution should contain only Co, Ni, and K salts. It should be a nearly saturated solution of $\text{KC}_2\text{H}_3\text{O}_2$, containing but little free acetic acid.

Sol.—Dissolved by H_2O , acids, NH_4 salts, NaCl , and most other Na salts. Insoluble in $\text{KC}_2\text{H}_3\text{O}_2$ and other K salts. Insoluble in dilute acetic, and in alcohol. The precipitate should be first washed with a 10 per cent solution of $\text{KC}_2\text{H}_3\text{O}_2$, and the latter salt finally removed by washing with alcohol.

Contam.—If Ca or other alkaline earths are present, a yellow NiCa nitrite, similar in properties (solubility, &c.) to the Co compound will separate. Pb also gives a similar compound. Care in washing off K salts is necessary.

Ign.—By addition of H_2SO_4 and ignition, the precipitate is converted to $3\text{K}_2\text{SO}_4 + 2\text{CoSO}_4$. One method of management consists in dissolving the washed precipitate through the filter with a little hot dilute H_2SO_4 into a weighed capsule, evaporating, and igniting. Some KHSO_4 may remain after ignition; removed by addition of a small lump of solid ammonium carbonate and igniting.

$\text{CoS.H}_2\text{O}$.

Rem.—For separation only. Properties essentially the same as those of $\text{NiS.H}_2\text{O}$. Precipitant, H_2S in weak

acetic solution or $(\text{NH}_4)_2\text{S}$. Oxidises readily in the air when moist, some sulphate being formed. Should be kept in contact with H_2S water during filtration.

Cond.—Absence of other members of $(\text{NH}_4)_2\text{S}$ or H_2S group. NH_4Cl assists the separation. Unlike $\text{NiS.H}_2\text{O}$, free NH_4OH does not materially influence the separation. Solution should be preferably slightly acid with acetic before filtration (*vide* $\text{NiS.H}_2\text{O}$).

Sol.—Formation of the precipitate prevented by moderate amounts of free acetic or mineral acids. When once formed, however, it is insoluble in these menstrua. Of the ordinary mineral acids, HCl has the strongest preventive effect, H_2SO_4 the least; but a very small amount of free H_2SO_4 retards the separation markedly. Soluble in hot HNO_3 or in aqua regia; also in KCy .

Contam.—Usually accompanied by Ni or other members of the group if not previously separated.

Ign.—Affords mixture of oxide (Co_3O_4) and sulphate.

Cu.

Rem.—Obtained by electrolytic deposition on platinum from acid solution. Free HNO_3 gives a bright coating. Too strong a current gives a spongy imperfectly adherent coat.

Cond.—Sulphuric acid solution preferable, with or without a few drops of nitric acid. Not over 8 per cent of free acid should be present. Chlorides disadvantageous. Organic acids (as citric, &c.) should not be present, since they afford a brittle deposit containing organic elements.

Sol.—Easily soluble in HNO_3 . When that acid is present at the end of the operation, flood out the dish with water before breaking the current. Deposit dissolved or prevented from forming by Cl, lower oxides of nitrogen, or too strong acid.

Contam.—If free HNO_3 is absent, As, Sb, or Bi may occur in the deposit, rendering it blackish. A black colouration is, however, sometimes due to other causes. If free HNO_3 is present, Zn, if present, begins to deposit (imperfectly) as soon as all the Cu is precipitated. Pb and Mn may separate from the solution on the other pole, as PbO_2 or MnO_2 , and in case a dish is used these oxides may fall to the bottom and be caught in the deposit. $\text{SnO}_2(x\text{H}_2\text{O})$ may also separate from the solution and be caught in the deposit in the same way.

Ign.—Easily oxidised by heating in air or oxygen. After deposition and washing with water, the water should be rinsed off with alcohol, the alcohol drained off, and the dish dried at a temperature which can be borne by the hand, not higher.

CuO or $3\text{CuO.H}_2\text{O}$.

Rem.—Usual precipitant, KOH or NaOH in a boiling solution or one subsequently boiled. Na_2CO_3 or K_2CO_3 may also be used in the same manner. The precipitate, at first the light bluish hydrate or basic carbonate, becomes black on boiling from elimination of H_2O .

Cond.—Alkaline solution, not containing bases, the hydrates of which are more or less insoluble. NH_4 salt and organic substances should be absent.

Sol.—Dissolved by acids, also by NH_4 salts and organic solutions, as citrates, &c. Precipitation prevented by alkaline bicarbonates, especially by KHCO_3 .

Contam.—Chiefly the alkali of the precipitant, which is washed out with great difficulty. Some SiO_2 dissolved by the reagent from the bottle in which it was kept, or otherwise introduced, may also be present. Left behind on dissolving in acid the ignited and weighed precipitate.

Ign.—Obtained as black CuO . Some reduction to the metallic form by contact of C may occur, but as the metal is not volatile it is readily restored by ignition with a few drops of HNO_3 . The use of platinum where reducing substances may be mingled with the precipitate is inexpedient. Precipitate quite hygroscopic after ignition.

CuS.

Rem.—Usually for separation. When for determination, treated as suggested under "*Ign.*" for production of

Cu₂S. Has ordinarily a brown to black colour, but when precipitated along with sulphur has an orange-red colour.

Cond.—Acid solution usually used, though not indispensable. Precipitation can be effected promptly in presence of moderately strong H₂SO₄, or of HCl if not too strong or hot. If HNO₃ is present, the solution must be dilute and cold.

Sol.—Soluble in hot dilute HNO₃ and in HCl when hot and moderately strong. Somewhat soluble in (NH₄)₂S, especially if polysulphides are present. Insoluble in HCl or H₂SO₄, or in NaHS, or KHS, unless polysulphides are present.

Ign.—Partly reduced to Cu with C. Converted to Cu₂S by mixing with sulphur and igniting in a current of hydrogen (in a Rose crucible).

PbSO₄.

Resm.—Usual precipitant, H₂SO₄. By digestion with alkaline carbonates or bicarbonates, it is converted to PbCO₃.

Cond.—Solution should be acid with H₂SO₄, and contain little or no free HNO₃ or HCl. The larger the proportion of these acids and the warmer the solution, the more H₂SO₄ required. NH₄ salts and salts of organic acids should not be present. Also, any large proportion of chlorides.

Sol.—Readily soluble in concentrated mineral acids, H₂SO₄, as well as the others, but less soluble in dilute H₂SO₄ than in pure water. Soluble in Na₂S₂O₃, in caustic alkaline solutions, and in ammonia salts, notably those of organic acids, especially when free ammonia is present. NH₄C₂H₃O₂ and (NH₄)₂C₆H₅O₇ may be used for this purpose. To obtain PbSO₄ for ignition and weighing, the usual procedure is to wash off all other substances with very dilute H₂SO₄, and then to remove the latter before drying by washing with alcohol.

Contam.—If all other sulphates (than PbSO₄) have not been removed by washing with dilute H₂SO₄ as just described, the precipitate may be contaminated with sulphates, most of which are insoluble in alcohol.

Ign.—Unchanged by a moderate heat. At temperatures usually higher than are ordinarily obtained with a Bunsen burner, the compound may fuse, but without volatilisation.

With C partially or entirely reduced to Pb, PbS, &c., which are volatile. The precipitate should be separated from the filter paper, which should be separately incinerated (in the cover of the *porcelain* crucible) with the aid of a few drops of concentrated HNO₃ and H₂SO₄, the ashes and the precipitate united and the whole ignited before weighing.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

November 6th, 1891.

Dr. E. ATKINSON, Vice-President, in the Chair.

MISS ALICE LEE, Mr. W. A. Shenstone, and Mr. Frank McLean were elected Members.

Prof. SYDNEY YOUNG, D.Sc., read a paper on "The Generalisations of Van der Waals Regarding 'Corresponding' Temperatures, Pressures, and Volumes," in which he gave the results of an investigation made with a view of testing whether these theoretical deductions agree with experimental facts.

From his virial equation—

$$\left(p + \frac{a}{v^2}\right)(v - b) = R(t + \alpha t),$$

Van der Waals showed that if the absolute temperatures of various substances be proportional to their absolute critical temperatures, their vapour pressures will be proportional to their critical pressures, and their volumes, both as liquid and as saturated vapour, will be proportional to their critical volumes. These deductions have now been put to the test of experiment.

Some years ago Prof. Ramsay and the author published data relating to the temperatures, pressures, and specific volumes of methyl, ethyl, and propyl alcohols, ether, and acetic acid. Since then, experiments have been made on benzene and its halogen derivatives, fluor-, chloro-, bromo-, and iodo-benzene, carbon tetrachloride and stannic chloride, and in a few cases the observations have been carried to the critical points.

The critical volumes being in many cases difficult to determine with any exactness, the author, instead of expressing the temperatures, pressures, and volumes of each substance in terms of their critical values, found it necessary to compare the various substances with one of them taken as a standard. Fluor-benzene was chosen as standard on account of the very simple relations observed between the mono-halogen derivatives of benzene, and the fact of its critical constants (temperature, pressure, and volume) having been determined with considerable accuracy.

Some of the critical constants of the various substances examined are given in the accompanying table, the brackets indicating calculated values.

Other tables of experimental data,—including boiling-points at corresponding pressures, vapour pressures at corresponding temperatures, molecular volumes of liquid, and saturated vapours at corresponding pressures and at corresponding temperatures,—and ratios calculated therefrom, accompany the paper. From these the author infers (1) that Van der Waals's generalisations are nearly true for chloro-, bromo-, and iodo-benzene, when compared with fluorbenzene; (2) that for benzene, carbon tetrachloride, stannic chloride and ether, the generalisations may only be taken as rough approximations to the truth, and (3) that for the three alcohols and acetic acid they do not hold good at all. The tables further show that more consistent results are obtained when the comparisons are made at corresponding pressures rather than at corresponding temperatures, particularly in the case of molecular volumes of saturated vapours.

The subject of saturated vapours is also treated by another method. If Van der Waals's deductions were strictly true, then the ratios of the actual densities of the saturated vapours of different substances to their theoretical densities should be equal at corresponding pressures. These ratios have therefore been calculated, and show an approximate agreement amongst benzene and its halogen derivatives, carbon tetrachloride, stannic chloride, and ether. For the other substances the agreement is less satisfactory. It is also noted that the ratio of the actual critical density to the theoretical density is for many substances about 4·4.

The alcohols differing so widely from the other compounds were compared amongst themselves instead of with fluorbenzene, with the result that somewhat closer agreement was found, but the deviations were still far outside the limits of experimental error.

Of the critical constants the volumes are the most difficult to determine, because at the critical point the curves connecting temperature and volume, and pressure and volume, are parallel to the axes of volume. Accordingly, the author in some cases has deduced this quantity by plotting against temperature, the numbers representing the ratios of the molecular volumes both of liquid and saturated vapour to those of fluorbenzene at corresponding temperatures and also at corresponding pressures. Four curves result which should intersect at the critical temperatures, and the point of intersection gives the ratio of the molecular critical volume of the substance to that

Substance.	Formula.	Temperatures. ° C.	Pressures in vapour of mercury.	Volumes in C.c.	
				Of a grm.	Molecular.
Fluorobenzene	C ₆ H ₅ F.	286.55	33.912	2.43	233
Chlorobenzene	C ₆ H ₅ Cl.	(360)	(33.912)	2.34	(262)
Bromobenzene	C ₆ H ₅ Br.	(397)	(33.912)	1.76	(275)
Iodobenzene	C ₆ H ₅ I.	(448)	(33.912)	1.47	(298)
Benzene	C ₆ H ₆ .	288.5	36.395	2.82	219
Carbon tetrachloride	CCl ₄ .	283.15	34.180		
Stannic chloride	SnCl ₄ .	318.7	28.080		
Ether	(C ₂ H ₅) ₂ O.	194.4	27.060		
Methyl alcohol	CH ₃ OH.	240.0	59.760		
Ethyl	C ₂ H ₅ OH.	243.1	47.850		
Propyl	C ₃ H ₇ OH.	263.7	38.120		
Acetic acid	CH ₃ .CO.OH.	321.6	43.400	2.46	147

of benzene. This method leads to results in fair accord with direct determinations.

In the discussion which followed the reading of the paper, Prof. RAMSAY said the results proved that Van der Waal's generalisations were only rough approximations, and he suggested that some force had been neglected, or a term omitted from the equations. Perhaps the assumption that the molecules are incompressible was not correct. He also strongly protested against the tacit assumption of the Van der Waal's laws, and deductions made therefrom, which had recently become so common, particularly in German text-books.

Prof. PERRY inquired whether the quantities *a*, *b*, and *c* had been determined for different substances and found to be constant.

Prof. RAMSAY said that for substances in states analogous to those of perfect gases the quantities were approximately constant, but when the liquid state was approached this was no longer true. According to Prof. Tait the two states were not continuous.

Prof. HERSCHEL remarked that Prof. Tait had established his law on the assumption that the co-volume is four times the volume occupied by the molecules. This law, he said, had been amply verified by experiments on explosions.

Dr. BURTON, referring to Prof. Ramsay's remarks on the compressibility of molecules, said the law of force between attracting molecules should be accurately known before any deductions were made; and he pointed out that at constant volume the pressure should be proportional to the absolute temperature if allowance be made for the negative pressure of attraction.

Mr. BLAKESLEY, in speaking of molecular forces, said he had observed that when water is allowed to evaporate from glass, a furrow is formed in the glass which marks out the original boundary of the liquid. To all appearances the particles of glass are torn away by the molecular forces acting along the boundary.

solids in liquids. He next takes up osmose, diffusion, the vapour pressures of solutions, their freezing-points, salt solutions, and the simultaneous action of several solvents.

The importance of a study of the laws of solution is fully shown in the author's concluding remarks. The laws of solution, he considers, resemble the laws of gases discovered towards the end of the last century, the one and the other being colligative in character. But the region included under solutions is far wider than that dealt with under gases. Innumerable substances are not met with in the gaseous state, whilst few indeed cannot be brought into solution, the silicates being the chief exceptions. Almost all the chemical processes occurring in Nature, in organisms as well as in the inorganic crust of the earth, are carried out between substances in solution. Hence the attention which chemists have recently paid to the phenomena and the laws of solution is not merely justifiable, but is necessitated by the present position of chemical science and its future prospects. There is no other work in the language in which this subject is discussed as ably and as fully.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxiii., No. 18, November 2, 1891.

Memoir by M. Armand Gautier accompanying the Presentation of his Work on Biological Chemistry.—The work is divided into five parts, in which the author expounds in succession the origin of the proximate principles and the mechanisms which give rise to them in plants and animals; the especial history of each of the chemical species which enter into the structure of organised beings; the composition of the tissues, humours, and secretions; the general functions which insure the life of each individual, and lastly, the mechanism of the general life, the sources which maintain the activity and the functioning of animals, and the relations established in them between the consumption of food and the transformation of its latent energy into heat, mechanical work, and growth. The author showed in 1877 that the green substances of plants hitherto confounded under the name of chlorophyll differ respectively among the dicotyledons, the monocotyledons, and the acotyledons. They even seem according to some analyses to vary in the different species of each class. He has given a method for preparing these substances in a pure crystalline state, and has shown that the chlorophylls produce by reduction a derivative which he called *colourless chlorophyll*, and which has since been known as protophylline. Reduced chlorophyll plays a very important part in the syntheses

NOTICES OF BOOKS.

Solutions. By W. OSTWALD, Professor of Chemistry in the University of Leipzig. Being the Fourth Book, with some Additions, of the Second Edition of Ostwald's "Lehrbuch der Allgemeinen Chemie." Translated by M. M. PATTISON MUIR, Fellow of Gonville and Caius College, Cambridge. London: Longmans, Green, and Co. 8vo., pp. 316.

In the Translator's notice we are informed that a systematic arrangement of the facts concerning solutions already established and a formal statement of the theory are to be found only in Prof. Ostwald's work. The theory of solution is, indeed, of very recent origin, and is chiefly due to the researches of van't Hoff. Prof. Ostwald considers in succession solutions in gases, solutions of gases in liquids, solutions of liquids in liquids, and solutions of

effected in the leaf. The author expounds in his work his views on the constitution of uric acid and of the bodies of the uric and xanthic series. The number of the known xanthic bodies has been increased from three (xanthine, sarcine, and guanine) to at least twelve. He has refuted the erroneous opinion that plants alone were capable of furnishing alkaloids, and shown, on the contrary, that in every animal cell which acts normally alkaloids are necessarily formed. He has also undertaken the study of the albumotoxines, which he considers intermediate between the ordinary albumenoids and the alkaloids properly so-called. In a different order of ideas he has shown that psychic work, the phenomena of consciousness, thought, and will, are not correlated with any expenditure of energy, mechanical, chemical, or thermic, but enter into a class of facts prepared solely by the physico-chemical acts, of which the nerve centres are the seat, but which are not commensurable with psychic acts.

Researches on the Monobromobutylenes.—E. Reboul.—The object of this memoir is to make known a new bromobutylene formed by eliminating HBr from ethylethylenebromide. Its structure is represented by the formula $\text{CH}_3-\text{CH}_2-\text{CBr}=\text{CH}_2$. It is a colourless liquid of an odour like garlic, and of the specific gravity 1.282 at +21°. It boils at 88° under a pressure of 0.759 metre.

The Direct Combination of Metals with Chlorine and Bromine.—Henri Gautier and G. Charpy.—Most metals, except aluminium, are scarcely attacked by dry chlorine and bromine at the ordinary temperature. It is very remarkable to see magnesium completely resisting the action of those liquids which attack aluminium. But if the action of the dry halogens is slow it becomes rapid in presence of water.

Contribution to the Physico-Chemical Study of the Function of the Kidneys.—C. Chabrie.—The first operation of the kidneys is a filtration analogous to that employed in the laboratory to separate a fine precipitate from the supernatant liquid. Secondly, the kidney acts as a dialyser. Urea, which has a small molecular volume, traverses the porous septa more rapidly than albumen, the volume of which is considerable.

Journal für Praktische Chemie.
New Series, Vol. xliii., Part 12.

The Formation of Sorbose.—A. Freund.—Sorbose is formed by the oxidation of a gelatinous substance contained in the berries of the service-tree.

Researches from the Laboratory of the University of Freiburg.—Ad. Claus.—These researches consist of a paper on absolute localisations by the transfer of paradinitro compounds into quinones.

Researches on Alloisomerism.—A. Michael and O. Schulthess.—A dissertation on the elimination of halogens in α - β ethers of haloid acids. The authors examine the action of zinc upon α - β -dibromopropionic ethers, upon α - β -dibromobutyric ethers, dibromosuccinic ethers, citra and itadibrompyruvic ethers, also upon α - β -trichlorbutyric ethyl ether.

Small Contributions from the Laboratory of E. von Meyer.—These comprise a paper by L. Harting on hexamethyleneamine, and one on acetone potassa and acetone soda by W. Vaubel.

New Series, Vol. xlii., Nos. 13 and 14.

Researches from the Organic Chemical Laboratory of the Technical High School at Dresden.—Communicated by Prof. R. Schmidt.—These researches include papers by R. Schmidt and H. Hähle on pyrocatechin carbonic acids, by H. Hähle on a new method of preparing phenoldicarboxylic acids, and by P. Otto on the action of chlorocarbonmonoxide upon glycolchlorhydrines.

Bismuth of Commerce and Purified Bismuth along with Remarks on the Atomic Weight of this Metal.—R. Schneider.—A controversial paper with reference to the recent memoir by Prof. Classen on the atomic weight of bismuth (*Journal*, xliii., 133). It does not admit of abstraction.

Contributions to the Chemistry of the Rhodium-Ammonium Compounds.—S. M. Jørgensen.—These include papers on the luteochodium salts, and on acid luteo- and roseo-nitrates.

Researches from the Laboratory of the University of Freiburg.—These consist of papers by C. Willgerodt and L. Ellon on the nitrohaloid-, hydrazo-, and nitrosohaloidazo-compounds; by Ad. Claus and W. Neukrantz on the oxidation of the mixed fatty aromatic ketones by potassium permanganate potassa, and by Ad. Claus and R. Wehr on paratolyl acetic acid.

Communications from the Chemical Institute of the University of Kiel.—These comprise a memoir by Th. Curtius on the nomenclature of organic compounds which contain two atoms of nitrogen in mutual combination. The author proposes that two atoms of nitrogen in simple combination, representing the quadrivalent radicle

$\begin{pmatrix} \text{N} \\ | \\ \text{N} \end{pmatrix}^{\text{IIII}}$, form the azi-group, to be written azine at the

end of a word. Two double combined atoms of nitrogen representing the bivalent radicle $\begin{pmatrix} \text{N} \\ || \\ \text{N} \end{pmatrix}^{\text{II}}$, form the well-

known azo-group, which at the end of a word is written azone. As soon as one of these radicles is partially or entirely saturated with hydrogen the syllable "hydr" is prefixed to "azi" and "azo." Thus we have the names "hydrazo" and "hydrazine," becoming at the end of a word "hydrazone" or "hydrazine." All possible bodies with two mutually combined atoms of nitrogen, such as the azo-, diazo-, and hydrazine compound, are derived from hydrazone (diimide, a body not yet obtained), or from hydrazine (diamide) by the substitution of hydrogen. Prof. Curtius also communicates a memoir on diammoniumsemisulphate.

Oxyderivatives of Alizarin Blue.—R. E. Schmidt and L. Gattermann.—The substances obtained are dioxyalizerin blue, formed by the action of fuming sulphuric acid of a very high percentage upon anthraquinone. Its composition is $\text{C}_{17}\text{H}_7\text{NO}_4(\text{OH})_2$. It is almost insoluble in ordinary solvents. In concentrated sulphuric acid it dissolves with a bright greenish blue colour, and the solution when examined with the spectroscopic shows two sharp absorption bands in the red and the orange. The vapour of this compound has a rich violet colour like that of iodine. Trioxalizerin blue, $\text{C}_{17}\text{H}_6\text{NO}_4(\text{OH})_3$, agrees in its spectrum with that of the quinoline derivative of alizarin bordeaux.

Transformation of Bibrom-succinic Ester with Zinc.—Ad. Claus.—A controversial paper not admitting of useful abridgment.

New Series, Vol. xlii., No. 15.

Lævulinic Acid and Acetondiacetic-dilacton.—Arthur Michael.—The author institutes a comparison between levulinic ethylethers obtained by different methods. He examines its behaviour with phenylhydrazine-hydrochlorate, with hydroxylamine, and the behaviour of acetondiacetic-dilacton with hydroxylamine and phenylhydrazine-hydrochlorate.

Appendix to Pyridinebetaine.—Dr. Krüger.—The author refers to his memoir on the pyridine bases, in which he mentioned that pyridinebetaine on treatment with sodium amalgam passes into a body which, in an alkaline solution, takes an intense blue colour if heated. The double bases formed by the addition products of

pyridine with methylethyl- and amyl-iodides display this blue colouration with remarkable intensity. The general result of the author's experiments is that all the pyridonium compounds formed by the addition of pyridine to halogenous substituted bodies of the fatty series, on reduction with sodium amalgam, zinc-powder, or a mixture of zinc and iron powder, in aqueous or alcoholic solution, yield a blue colour. This coloured reaction is a convenient means of ascertaining whether a body under examination can be a pyridonium compound or not.

Ring and Nucleus Formation of the Carbon Compounds.—W. Vaubel.—This memoir cannot be usefully reproduced without the accompanying diagrams.

Constitution of Cymol.—M. Filetti.—The author's experiments confirm fully the assertions of Widman; cymol does not contain normal propyl, but is an isopropyl derivative. The assumed transformations of the propyl group in the cumic and cymol series is thus deprived of all foundation.

The Degree of Concentration of Solutions as Determined by their Refractive Power.—H. O. G. Ellinger.—The author considers the oleorefractometer of Amagat and Jean as especially adapted for such determinations, but thinks "differential refractometer" a more suitable name. His results are given in a tabular form.

Optical Analysis of Butter Fat.—H. O. G. Ellinger.—If natural butter, which gives the highest value (35°) is mixed with equal parts of margarine, the reading obtained is 21½°, that is, it falls below the lowest figure of natural butter (23°). The optical method thus fully detects a sophistication with any quantity of margarine not less than 45 per cent.

On Polymeric Trichloroacetonitril.—N. Tschervew-Iwanoff.—The polymerisation is effected by the prolonged action of dry hydrochloric acid and exposure to light.

Revue Universelle des Mines et de la Metallurgie.

Series 5, Vol. xv., No. 1.

Application of the Basic Process to Refining Copper.—Percy E. Gilchrist.—From the *Journal of the Society of Chemical Industry*.

No. 2.

Detection and Determination of Aluminium in Cast Irons and Steels.—A. Carnot.—Taken from the *Comptes Rendus*, and already noticed.

Determination of Silica in Presence of Iron.—M. Leclerc.—Already noticed under the *Comptes Rendus*, from which it is taken.

MISCELLANEOUS.

The Crystal Palace Electrical Exhibition.—A meeting of the Honorary Council of Advice, and of the Special Committee appointed by the Electrical Section of the London Chamber of Commerce, will, by kind permission of the Lord Mayor, be held at the Mansion House at 3 o'clock on Wednesday, the 25th inst., when a report on the progress of the Exhibition will be presented, and the question of how the Exhibition may best be used as a means of advancing the interests of electrical science will be considered. The Lord Mayor will preside. The whole of the space is now practically allotted, extra buildings having been erected for certain large installations which could not otherwise have been accommodated.

Optical Determination of the Quantity of Albumen in Urine.—H. O. G. Ellinger.—By means of the oleorefractometer of Amagat and Jean (differential refractometer) the author has determined the quantities of albumen in urine with approximate accuracy.—*Journal für Prakt. Chemie*.

MEETINGS FOR THE WEEK.

WEDNESDAY, 25th.—Society of Arts, 8. "Measurement of Lenses," by Professor Silvanus P. Thompson, F.R.S. Geological, 8.

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THE CHEMICAL NEWS.

VOL. LXIV., No. 1670.

STUDIES ON SAPONIFICATION.

No. I.

By ALFRED H. ALLEN.

IN a recent number of the CHEMICAL NEWS (vol. lxiv., p. 201), Mr. J. A. Wanklyn took strong exception to my statement (p. 179) that Messrs. Wanklyn and Fox had never published a single original experiment in support of their assertion that the proportion of glycerin yielded by the saponification of butter and other fats exhibits any grave departure from the amount required by the accepted view of their constitution. Mr. Wanklyn pointed out a fact of which I was fully aware, but had omitted to mention through inadvertence, namely, that in January last he read a paper before the London Section of the Society of Chemical Industry, in which he described an experiment which he considered proved that butter yielded only 6.2 per cent of glycerin on saponification, instead of the 11 or 12 per cent which is required by the ordinary theory and which agrees with the determinations of various observers.

Mr. Wanklyn lays much stress on his experiment—the only one of the kind he has published—as affording proof of his ingenious but otherwise unsupported isoglyceride theory, which I fully described in a paper recently published in these columns (p. 179).

As Mr. Wanklyn complains of his experiment having been left unnoticed by me, and believes that chemists will find great difficulty in resisting the conclusion which follows from the experiment, I propose to submit it to a critical examination, and to show that Mr. Wanklyn's

50 grms. of butter-fat was mixed with 9.42 grms. of dry slaked lime, and the mixture heated in an open dish at 100° C. for a long time and constantly stirred. 6.46 grms. more slaked lime was then added, the mixture treated with boiling water, and the liquid filtered.

Aqueous extract was neutral in reaction. Evaporated it left **residue** weighing—

Residue.—Treated with boiling alcohol and liquid filtered.

Alcoholic Extract.—Evaporated, left **residue** weighing 4.606 grms. This when treated with water and the liquid filtered gave—

Solution, evaporated, gave **resid.** weighing—

Residue, consisting of insoluble lime salts, &c., was apparently not further examined.

Residue (by difference) weighed—

1.991 gm.

1.405 gm.

3.201 gm.

These two residues together contained 0.300 of lime, determined, leaving—
3.096 grms. of "glycerin."

Said to contain no unchanged butter. Apparently not further examined.

published account of it (*Journ. Soc. Chem. Ind.*, x., 89) contains abundant internal evidence of its inconclusive nature.

Mr. Wanklyn's experiment was based on the saponification of butter-fat with slaked lime; the solution of the resultant glycerin from the product by water and alcohol, evaporation of these solutions, and weighing of the residues. In one or two respects Mr. Wanklyn's mode of procedure is implied rather than actually expressed, but the accompanying table represents what I understand him to have done, and I believe is an accurate statement of the facts.

The foregoing is a synopsis of Mr. Wanklyn's procedure and results, but it is necessary to describe them more fully, and in doing this I shall, whenever possible, make use of Mr. Wanklyn's exact words.

To commence with, I may say that Mr. Wanklyn stated that the butter he employed came direct from one of the best London dairies, and that he quite appreciated the necessity of making sure of the genuineness of the material. It may therefore fairly be assumed to have been of normal character.

In making his experiment Mr. Wanklyn "took 50 grms. of butter with 9.42 grms. of dry hydrate of lime, making a total of 59.42 grms. These materials were placed in a platinum dish provided with a stirrer, and the vessel with its contents was heated on the water-bath and constantly stirred for a long period. From time to time it was allowed to cool, and was then weighed, five times in all. There was a steady loss of weight, and ultimately the weight of the compound fell to 58.510 grms., showing a loss of 0.910 gm. of water."

Mr. Wanklyn then points out that "hydrate of lime and a glyceride react without production of water, yielding only lime salts and glycerin. The loss of water could arise from two sources; either from the action of free fatty acid in the butter, or from the action of lime on an isoglyceride." Mr. Wanklyn states that "possibly there is a third way" in which water might be formed, but does not say what it is. I suggest the well-known reaction $\text{CaH}_2\text{O}_2 + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{O}$.

Mr. Wanklyn makes the bold assumption that no loss of glycerin will occur when a mixture of glycerin, slaked lime, and fatty acid salts of lime is heated for a long period to 100° C. in an open dish with constant stirring. This is so opposed to the known behaviour of glycerin under somewhat similar conditions that it should have been *proved*, and not simply *assumed*, to be the fact. If glycerin volatilised during the first stage of Mr. Wanklyn's experiment, the whole value of the operation, which was to prove deficient production of glycerin, is nullified. As a matter of fact Mr. Wanklyn observed a loss of 0.910 gm., which he assumed, but did not prove, to have been due to the evaporation of water formed by one of the reactions indicated.

Throughout his paper Mr. Wanklyn does not appear to contemplate the possibility of the absorption of atmospheric carbonic acid by slaked lime exposed to the air and constantly stirred. If this occurred, and glycerin as well as water volatilised, the actual loss of glycerin was considerably in excess of the loss of weight observed.

Mr. Wanklyn then added to his product a further quantity of 6.46 grms. of hydrate of lime, although the amount previously used was more than equivalent to the fatty acids of the butter. Why the second addition was made is not stated and is not apparent, nor does Mr. Wanklyn state whether he continued the operation of heating and stirring the mixture after adding the further quantity of lime. My impression is that he did.

Mr. Wanklyn next digested the mixture with 600 c.c. of water, using the solvent boiling and in successive portions. The undissolved portion was treated with 300 c.c. of boiling alcohol, which was evaporated in its turn; the residue obtained being weighed and then apparently treated with water, and the filtered liquid again evaporated. How much glycerin was lost by evaporation

during the latter stages of the process of concentrating the aqueous and alcoholic liquids is of course unknown. That dilute solutions of glycerin can be concentrated to a considerable extent without loss is admitted, but the accepted view that glycerin volatilises from its concentrated solutions at 100°, and is itself volatile at that temperature, is based on too many observations to be ignored or pooh-poohed, unless rigid experimental demonstration be afforded showing that previous observers have been in error. This proof Mr. Wanklyn does not furnish.

The following are Mr. Wanklyn's results:—

	From 50 grms. of Butter.	= per cent.
Aqueous residue	1'991	3'982
Alcoholic residue { Soluble	1'405	2'810
Insoluble	3'201	6'402
Insoluble lime salts	58'140	
	64'737	

The material that produced them.. .. . 64'970

Mr. Wanklyn points out that the agreement between the weight of the materials taken and the products was very close, showing that "nothing important had escaped by evaporation or was otherwise lost."

Mr. Wanklyn states that the aqueous extract was not alkaline, which "shows that the whole of the hydrate of lime was used up, and that perfect action must have taken place; and for every equivalent of butter acids there were two equivalents of lime." As a matter of fact the proportion of lime used was sensibly in excess of two equivalents; twice the quantity requisite to effect the saponification of 50 grms. of average butter being 14'98 grms., whereas Mr. Wanklyn employed 15'88 grms. Mr. Wanklyn gives no clue to what used up the second equivalent, to say nothing of the excess of lime. Perhaps it combined with atmospheric carbonic acid, absorbed while the mixture was being heated, with constant stirring, in an open dish on the water-bath for a long period; but if so, what becomes of the argument from the approximate concordance between the weight taken and that of the product obtained? If carbonic acid was gained, something—perhaps glycerin—was lost in addition to the displaced water of the slaked lime, or the weight would have increased instead of somewhat diminishing. The fact that the aqueous solution of the product was not alkaline, although excess of lime was used, goes rather to prove extensive absorption of carbonic acid, and the care with which Mr. Wanklyn stirred, than that all the lime (second equivalent and excess) had reacted with the butter.

Mr. Wanklyn regards the difference between the weight of the material taken and the products obtained (amounting to 0'233 grm.) as having been due to the formation and volatilisation of butyric ether. But if saponification was complete, and the exhaustion of the product with water was perfect, all butyric acid must have been dissolved as calcium butyrate. How, then, can Mr. Wanklyn account for the formation of butyric ether? It could not have been formed during the treatment with water, for there was then no alcohol present; and it could not have been formed in the alcoholic treatment, for all butyrate must have been previously dissolved by the water.

This brings us to the next anomaly. Thousands of analyses by scores of observers have proved that butter yields on saponification about 5½ per cent of butyric acid. Whether the source of that acid be a glyceride or iso-glyceride is immaterial. Now 5'5 per cent of butyric acid corresponds to 6'688 of butyrate of calcium, which is a salt soluble both in water and alcohol. It is more soluble in cold water than in hot, but readily in either, and should certainly have been dissolved out by the repeated treatments with water and alcohol to which Mr. Wanklyn subjected his product of saponification. But

Mr. Wanklyn's soluble extract only amounted to 6'792 per cent, so that if he dissolved out all his butyrate of calcium he only obtained 0'104 of glycerin, instead of 6'2 per cent, which he admits and claims to have obtained. But that Mr. Wanklyn did not dissolve out all the calcium butyrate which must have resulted from complete saponification is evident from the amount of lime in his soluble extracts, which he "determined in each case by actual experiment," and found to be "about 3 decigrammes."

Now 0'300 of lime represents 1'146 grms., or 2'292 per cent, of calcium butyrate, which is the amount Mr. Wanklyn apparently obtained in solution, against 6'688 per cent which he ought to have obtained. But it is curious that Mr. Wanklyn did not calculate the lime he found in his extracts to calcium butyrate, and deduct this from the weight of the residues in order to deduce the glycerin; especially as he had observed that the aqueous extract was not alkaline in reaction, and therefore that the lime existed as a neutral salt. It is an astounding fact that throughout the description of his experiment Mr. Wanklyn completely ignores the formation of butyrate of calcium! His results might have been yielded by tallow instead of butter, for all the figures show to the contrary. I imagine that only on the ground that butter yields an insignificant proportion of butyric acid on saponification can Mr. Wanklyn justify his omission to calculate his lime to butyrate before deducing the weight of glycerin from his result. Mr. Wanklyn did at one time hold this heterodox view, although other chemists were daily obtaining results showing the formation of 5 to 6 per cent of butyric acid; but Mr. Wanklyn now himself admits the errors of his former views, and has formulated his iso-glyceride theory to account for the accepted fact of the production of butyric acid in considerable proportion.

Assuming Mr. Wanklyn to have succeeded in effecting complete saponification, he is on the horns of a dilemma. (a.) If his calcium butyrate was wholly dissolved, then his lime determinations were wrong; and there was only an insignificant quantity of butyric acid produced. (b.) If his lime determinations were correct, he only dissolved out about one-third of the total calcium butyrate; and if he failed to dissolve the remainder, what guarantee is there that he was any more successful in extracting the glycerin? The only way out I can imagine for Mr. Wanklyn would be for him to suppose the formation of a basic butyrate of calcium by the action of the second equivalent of lime, and the insolubility of this hypothetical compound both in boiling water and in alcohol. A salt having such properties would be very valuable to those desiring to determine butyric acid. But even this resource appears to fail; for I have added to butyric acid prepared from butter twice the quantity of lime-water requisite to convert it into the neutral butyrate of calcium, evaporated the liquid to dryness, and taken up the residue with water. The insoluble portion effervesced strongly with dilute sulphuric acid, and, when the filtered liquid was distilled, the distillate contained only a mere trace of butyric or other volatile acid.

Correcting the amount of soluble extract (=6'792 per cent) obtained by Mr. Wanklyn by the calcium butyrate (2'292 per cent), corresponding to the lime determined in the extract, there is only 4'500 per cent of glycerin obtained in the experiment, or a little more than one-third of the amount which should have been found if butter possessed the character of an ordinary glyceride. But Mr. Wanklyn only obtained a little more than one-third of the proper amount of butyrate of calcium, so that it really seems probable that he only succeeded in saponifying something like one-third of the butter employed. This suggestion explains the results from one point of view, but Mr. Wanklyn urges that saponification must have been complete, (1) because all the lime had been used up, and (2) because boiling alcohol did not dissolve out of the product any unchanged butter. The first of these observations I have already shown is no

proof of complete saponification and to be susceptible of another explanation. As to the second argument, it may fairly be asked why the alcohol should be expected to dissolve the unchanged butter, when Mr. Wanklyn did not succeed in dissolving the far more soluble calcium butyrate by repeated treatments with water and alcohol? But is Mr. Wanklyn *quite sure* that no unchanged butter was dissolved out by the treatment with alcohol? He got a total alcoholic residue of 4.606 grms., or 9.212 per cent, and of this 3.201 grms., or 6.402 per cent, was insoluble in water. This portion presumably consisted of calcium salts of higher fatty acids; but how does Mr. Wanklyn know that it contained no admixture of unchanged butter? He does not say that he determined the lime in it or examined it in any other way.

The same doubt applies to the insoluble lime salts remaining after treatment of the product with water and alcohol, which Mr. Wanklyn appears to have left unexamined. It is to be regretted that he did not take the obvious precaution of decomposing these insoluble lime salts with acid, and seeing how far the fatty substance which separated consisted of free fatty acid, and how far of unchanged glyceride. But possibly Mr. Wanklyn's omission to do this was due to his peculiar and strictly personal difficulty in distinguishing a free fatty acid from a glyceride; for in the discussion on the very paper, "On the Constitution of Butter," in which Mr. Wanklyn described his lime experiment, he declined to pronounce an opinion as to whether or not butter-fat contained free fatty acids! (*Journ. Soc. Chem. Ind.*, x., 92). I trust Mr. Wanklyn will forgive the suggestion that the attention he has given to other branches of chemistry has prevented him from keeping abreast with the improvements in the analytical methods of examining fats which have been so numerous during the last few years; one of which, in daily use in many laboratories, would have enabled him to detect and determine the proportion (in terms of any acid he might prefer) of free fatty acids inside of twenty minutes.

So far I have purposely confined myself to a criticism of Mr. Wanklyn's one experiment: I next propose to describe my own experience in repeating it, and the other experiments which have suggested themselves in connection with it.

Sheffield, November 16, 1891.

DETERMINATION OF FATTY MATTER IN DAIRY PRODUCE.

By MM. LEZÉ and ALLARD.

In the Session of March 24th, 1890, M. Lezé communicated to the Academy of Sciences a new process for determining the fatty acid of milk.

This process consists in heating in a flask a mixture of the milk to be analysed with 4 or 5 vols. of pure concentrated hydrochloric acid; the caseine which is at first precipitated re-dissolves in the excess of acid, the fatty matter is isolated and collects in oily drops on the surface of the liquid. The acid is then neutralised with ammonia diluted with half its volume of water, and so much warm water is added that all the fatty matter appears in the neck of the flask.

This neck, which must be narrow and long, is divided into c.c.'s and tenths of a c.c.; the flask is kept for some time in a stove at 40°, and the volume of the fatty matter is read off, which, multiplied by the specific gravity of this matter at +40°, gives the weight of butter for like of milk.

The temperature of +40° has been selected because at this heat the butter remains melted and homogeneous; its density is then = 0.90.

The author's recent researches have been directed to

the generalisation of this process for the determination of the fatty matter.

We have recognised at first that the separation of the fatty matter is always effected better if, in the treatment with hydrochloric acid, the acid is allowed to react upon the milk for several hours, preferably at a temperature of 25° to 30°. The reactions of caseine always take place slowly, and too hasty heating of the mixture of the two liquids when recently formed may cause an imperfect separation. The gentle heat merely collects the drops of the liquefied fatty matter.

The hydrochloric acid must be absolutely free from uncombined chlorine: if this condition is not observed there ensues a precipitation of flocculent matter and an escape of gas, which render it more difficult to read off the volume of the butter. The neutralisation with ammonia may be dispensed with, and smaller flasks may be employed.

We have examined if the fatty matter was really butter and had not undergone any chemical modification. In the stove it undergoes merely an insignificant loss; no trace of water is separated, and no residue is left on incineration.

We have found that by means of this reaction we may easily determine the fatty matter in creams, cheeses, and in margarines.—*Comptes Rendus* (vol. cxiii., p. 654).

ARSENICAL WINE.

In a document handed in to a recent "Œcumenica Congress" the Editor of an influential London literary journal complained that "the modern mind had so steeped itself in Science that its faculties in other directions were blunted." But we may well question whether this steeping has led to saturation if we read the report of a late coroner's inquest in Sussex. A gamekeeper had obtained possession of an empty arsenic cask, and, as a medical contemporary informs us, utilised it for the storage of some home-made wine! The liquid took up, in consequence, nearly 6 grs. of arsenic per fluid ounce, and the first glass imbibed proved fatal.

On the inquest it appeared that the cask had contained a preparation known as "weed-killer." Large quantities of arsenic, it was stated, are used for this purpose by gardeners and farmers. Gamekeepers are not generally reputed as being the most enlightened part of Her Majesty's subjects—witness the sages who contended that the cuckoos all turned into hawks at the end of summer. But in ignorant recklessness the Sussex victim certainly deserves distinction.

But for such casks to be in the hands of an ignorant rural population is a great misfortune. Arsenic, no doubt, will kill weeds and the Colorado beetle as readily as it will gamekeepers. But there are other safer and equally convenient preparations which will rid garden-paths of weeds. As an instance we may mention the drega from the preparation and storage of "nitrate of iron." This preparation, which is sometimes too abundant at chemical works, might safely be sold as a weed-killer. That it will destroy vegetation we know from observation, whilst if it should be accidentally scattered upon any esculent fruit or vegetable it can do little harm, especially as its abominably astringent taste would at once cause its rejection. But if the dust of an arsenical preparation is scattered over fruits and vegetables, neither the taste nor the colour will give any warning.

We quite agree with the suggestion of the Sussex jury that casks containing arsenic or arsenical preparations should be branded as a warning against their use afterwards. But the substitution of a less deadly preparation for horticultural and agricultural uses would certainly be a "more excellent way."

DETERMINATION OF SMALL QUANTITIES
OF ALKALI AND RECOGNITION
OF THE NEUTRALITY OF WATER.

By F. MYLIUS and F. FOERSTER.

(Continued from p. 255).

Preparation of the Solutions necessary for the Colorimetric Determination of Alkali.

THE first step is the preparation of pure ether. The ether of commerce is ordinarily acid. Its purification is generally effected by shaking with dilute soda-lye. Besides acids other impurities are thus removed. The ether thus treated is then once more shaken up with water and preserved over water, as it is used only in an aqueous state. It is then easily possible to remove by shaking any trace of acid which has been formed on long standing. The formation of acid takes place very slowly, so that it cannot occasion any error during the course of an operation. For preparing the ethereal solution of eosine 0.1 grm. of the pulverised colouring-matter, previously dried at 100°, is dissolved in 1 litre of aqueous ether. The solution requires several hours. If there are added to the solution a few c.c. of water they must assume on shaking a red tone in proof of the absence of acid. An alkaline solution of eosine is also necessary for effecting the colorimetric determination. It is obtained by dissolving 0.01 grm. iodeosine in a small excess of soda-lye (0.24 c.c., using 0.4 c.c. of 4.10ths soda-lye) and diluting the solution with water to 1 litre. If exposed to light it is decolourised in time, and must therefore be kept in brown bottles in a dark place.

For our experiments it was necessary to procure neutral water. For this purpose we used a distillatory apparatus of the following construction:—A round platinum flask containing 200 c.c. is connected at the top by means of a capital with a refrigerating worm. This consists also of platinum, so that the water during refrigeration comes in contact with no other material. The flask is heated by an annular burner. It terminates below in a platinum tube bent at right angles, connected at a convenient point with the efflux tube of a glass flask, which is also bent at right angles. Both vessels are at the same level, so that the height of the water in the glass vessel shows that in the platinum flask. A continual influx of water during the distillation is effected by a large Mariotte's vessel, the outflow tube of which is at the constant level.

If the apparatus is fed with distilled water, the distillate obtained, if collected in a platinum vessel, is free from solid impurities, but contains demonstrable traces of ammonia. To keep these back a small addition of sulphuric acid or of an acid sulphate is commonly employed. Phosphoric acid is unsuitable. If the water to be distilled was acidulated with a solution of vitreous phosphoric acid so as to redden litmus-paper distinctly, the first portions of the distillate were almost free from ammonia; but as the distillation continued, and the meta-phosphoric acid passed into ortho-phosphoric acid, the distillate became gradually richer in ammonia, so as to excite the suspicion that the vitreous phosphoric acid contained ammonia as an impurity. This was in fact the case, as Nessler's reagent gave the characteristic brown colour in the alkaline solution of the acid.

In our experiments 0.05 grm. pure sulphuric acid were quite sufficient to keep back the volatile bases in the platinum vessel even when the distillate amounted to several litres. Water thus obtained takes up, according to a number of experiments, for 100 c.c. as much eosine (0.054 m.grm.) as corresponds to 5.4 c.c. of the alkaline solution of eosine.

The objection might be raised that in our process a small portion of the sulphuric acid might have been carried over with the watery vapour. We sought to meet this objection by re-distilling the water in the same apparatus with pure soda. Repeated experiments showed

that the water thus re-distilled had the same eosine value as that distilled with sulphuric acid. The colour obtained in the eosine test corresponded on the average to 5.9 c.c. of the alkaline eosine solution. The difference of 0.5 c.c. which appeared on testing both kinds of distillates corresponds very closely to the mean experimental error, so it may be assumed that no appreciable transfer of sulphuric acid or of soda takes place during distillation. If a trace of sulphuric acid passes over it is certainly less than 100,000,000th part of the water.

We have hitherto not taken especial note of the impurities which the water takes up as it drops from the ambient air. We may call a water neutral which on the eosine test, according to our method, becomes coloured like a liquid which in 100 c.c. contains 5.65 of the alkaline solution of iodeosine.

In carrying out the more delicate alkalimetric investigations, it is often inconvenient first to procure pure water by distillation. It is generally sufficient to neutralise ordinary distilled water with sulphuric acid, so as to reach the "eosine value" of neutral water (5.6—5.7 c.c. of eosine solution in 100 c.c. of water).

The colorimetric determinations are best effected as follows:—Into a globular parting funnel holding about 150 c.c. there are introduced 100 c.c. of the water in question; 20 c.c. of the ethereal solution of eosine are added and well shaken. The aqueous reddened stratum is thus enlarged by taking up ether to 110 c.c.

(To be continued.)

ON THE ESTIMATION OF SULPHUR.

By GEORGE CRAIG.

EVOLUTION methods, whereby the substance to be determined is first of all eliminated as a gas from the material under examination, must always be more satisfactory than gravimetric methods, although no greater degree of accuracy is attained thereby. Such, for instance, is the estimation of NH_3 by liberation with alkali, with subsequent condensation and titration with standard acid.

Sulphur, when it exists as monosulphide, decomposable by HCl , is certainly best determined after expulsion as H_2S .

Pig-iron and steel, even when containing Cu , yield all their S as H_2S on treatment with HCl , which, as I proposed in 1881, may be completely oxidised to SO_3 by passing the gases through ammoniacal H_2O_2 .

In blast-furnace slags the S exists wholly as CaS , which, it must be borne in mind, readily oxidises when the finely ground slag, especially from hematite iron, is kept for any time. The only correct method whereby it can be estimated, unless with the expenditure of much time and labour, is by decomposing the slag with HCl and estimating the S in the H_2S evolved. For this purpose I use the apparatus shown in Fig. 1, which scarcely needs explanation. 20 grs. of finely ground slag is heated with 1 oz. of boiled water, and the air expelled from the flask by a current of coal-gas which has been passed through a mixture of KHO and H_2O_2 in the Liebig's bulbs shown. When boiling agitate so that the slag is all in suspension, and add HCl by means of the 3-way stopcock, continuing the agitation until the slag is all decomposed, which takes place in a few seconds; boil, and pass a current of the purified coal-gas through the apparatus with the aid of the aspirator. The nitrogen bulb—containing 100 grs. H_2O_2 , 200 grs. NH_4HO —is preferably made, as in figure, by cutting the escape-tube nearly at the bulb, widening the orifice, introducing some glass beads, and connecting with I.R. tubing as shown. The contents of the nitrogen bulb are washed into a small beaker, heated to boiling, acidified, and the SO_3 established as BaSO_4 as usual.

It is now more than a year since it occurred to me that

FIG. 1.

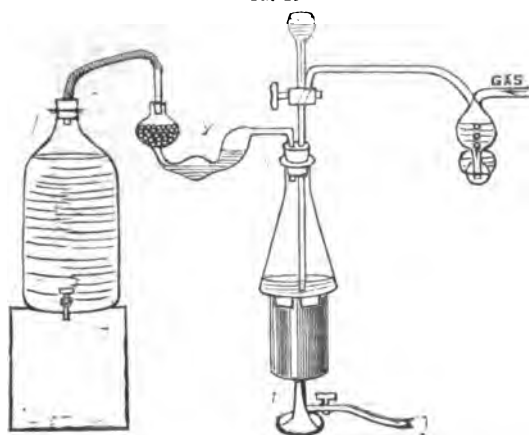


FIG. 2.

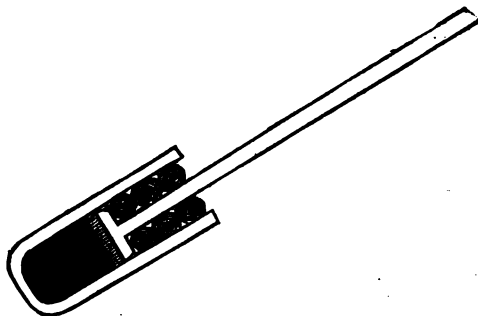
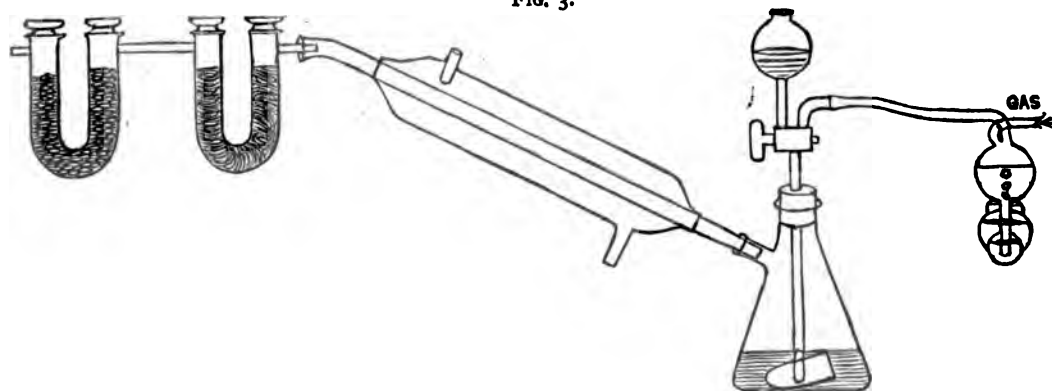


FIG. 3.



compound sulphides, such as pyrites, &c., might be made amenable to this evolution process also, by the simple preliminary operation of heating with zinc-dust, and so reducing to the state of monosulphides. In a recent number of the *CHEMICAL NEWS* there is a translation from the *Berichte* of an almost identical process; but as reduction with zinc is very much simpler, a description of the method I employed may be of interest.

Ordinary zinc-dust, after passing through a fine sieve, is heated to redness to expel moisture and occluded hydrogen, and allowed to cool out of contact with air; a tube of Bohemian glass closed at one end suits admirably for this purpose.

Ten or twenty grs. of the pyrites in fine powder are weighed into a small ignition tube of Bohemian glass (2" long, $\times \frac{1}{8}$ " diam.), then five times its weight of zinc-dust added, intimately mixed with a platinum wire, the surface levelled by tapping gently, and covered with a layer of zinc-dust. A stout glass rod, about 8" long, had one end flattened out into a disc that entered easily into the little decomposing tube. This was introduced until the disc rested lightly on the covering layer of zinc-dust, and the upper portion of the tube was packed with asbestos yarn firmly enough to enable the glass rod to serve as a support (Fig. 2). The tube and contents is then revolved over an argand flame until thoroughly heated, and then over a Bunsen flame. In a few seconds bright incandescence takes place, and after maintaining at a red-heat for thirty seconds longer it is withdrawn gradually, revolving all the while, and then allowed to cool.

When carried out in this manner practically no sulphate is reduced, but when maintained at a red-heat for five to ten minutes all sulphates are reduced. Apropos of sulphates in pyrites, I have not seen it recorded that a considerable amount of pyrites may be oxidised while grinding the sample in the agate mortar; in the dark a red glow follows the track of the pestle.

After withdrawing the support and asbestos packing the tube is dropped into a 4-oz. conical flask with side-tube, connected with condenser and U-tubes, as shown in Fig. 3. The first U-tube contains CaCl_2 , and the second is filled with glass beads and contains 100 grs. of NaHO solution (1000 grs. and 1500 grs. water). 1 oz. boiled water is added, and a current of purified coal-gas passed through apparatus. Heat is applied and the HCl gradually run in until decomposed, contents boiled, and apparatus washed out with a current of gas. I preferred to estimate the H_2S by washing out the U-tube (without removing stoppers) into a beaker, adding excess of FeCl_3 , agitating, acidifying with HCl delivered at bottom of liquid by means of a pipette, heating until all FeS decomposed, and titrating with bichrome. The ideal process would be to accurately weigh the NaHO solution and titrate after absorption with acid, using an indicator neutral to NaHS or Na_2S . The arsenic I found was completely expelled, so that not a trace could be detected in the combined residues from a number of experiments.

PROPERTIES OF PRECIPITATES, &c.*

By E. WALLER, Ph.D.

(Continued from p. 259).

PbCrO₄.

Rem.—Usual precipitant, $K_2Cr_2O_7$ in solution acid with acetic.

Cond.—Bi, Ba, Ag, and Fe should not be present. Solution should not contain chlorides or large amounts of alkaline salts, and should be acid with no stronger acid than acetic. Alkaline citrates, tartrates, &c., should be absent.

Sol.—Dissolved by moderately strong mineral acids and by caustic alkalis. HCl reduces the chromium partially or entirely to Cr_2Cl_6 , more readily in the presence of acetic acid, alcohol, or other carbon compounds. Soluble in hot moderately concentrated solutions of $(NH_4)C_2H_3O_2$. Insoluble in very dilute HNO_3 .

Contam.—Possibly Ba, Bi, or Hg, chromates, &c. If much Fe is present, the precipitate is likely to contain that element, probably as $Fe_2(CrO_4)_3$.

Ign.—Alone fuses and parts with some oxygen. With C it is more easily decomposed, some metal being reduced. On account of these properties the precipitate is usually dried on a weighed filter for estimation. The Gooch filter, in which, if paper is used, it need be only about the size of a five cent piece, is especially advantageous for this purpose.

PbS.

Rem.—Usual precipitant, H_2S . Partially decomposed by drying at $100^\circ C$. Used for separation.

Cond.—Solution may be slightly acid, neutral, or alkaline. HCl interferes most with complete separation, HNO_3 less, and H_2SO_4 least. If the solution is acid with any large proportion of these, the precipitation is best effected in the cold.

Sol.—Dissolved by dilute boiling HNO_3 , though that solvent almost invariably affords some $PbSO_4$. Of concentrated acids hot HCl is the best solvent, since with either HNO_3 or H_2SO_4 some $PbSO_4$ will form in such a way as to protect a portion of the sulphide. Soluble in $Na_2S_2O_3$.

Ign.—Volatilised. Easily reduced to metal by ignition with C.

AgCl.

Rem.—For determination of Ag, usual precipitant HCl. For determination of Cl, usual precipitant $AgNO_3$. Separates most readily in presence of an excess of silver salts. Partially decomposed by heating with strong HNO_3 or H_2SO_4 . Darkens in strong daylight, more quickly in sunlight, but may become very dark without material loss of weight.

Cond.—Acid solution, absence of any notable quantities of alkaline chlorides or other alkaline salts.

Sol.—Partially dissolved by moderately strong and hot HCl or HNO_3 . Somewhat soluble in alkaline and alkaline earth chlorides and nitrates. Readily soluble in NH_4OH , in KCy, and in $Na_2S_2O_3$. In the latter, less readily if the substance has been changed by light.

Ign.—Fuses at a low temperature (dull red) and volatilises at a little higher temperature. Easily reduced to metal by strong heat, especially when mixed with Na_2CO_3 or C. On burning the filter-paper (which should be separated from the precipitate) the ash should be treated with HNO_3 to obtain $AgNO_3$, then a drop or two of HCl is added to restore AgCl, and the whole after drying cautiously heated to incipient fusion.

As₂S₃.

Rem.—Usually precipitated by H_2S in HCl acid solution. From the solution of arsenic sulphides in alkaline polysulphide, the addition of acid separates As_2S_3 .

As_2S_3 requires very thorough drying before weighing, the last portions of water being driven out with difficulty.

Cond.—Solution acid, with some mineral acid (HCl preferable). As should be in triad form. If in pentad form it is slow to reduce and precipitate ($As_2S_3 + S_2$) by prolonged action of H_2S and warming.

Sol.—Dissolved by alkaline solutions (hydrates, carbonates, or sulphides), also by aqua regia, fuming nitric acid, water solutions of chlorine, bromine, &c. In a neutral solution scarcely any precipitation occurs. Insoluble in strong HCl, even on boiling. Practically insoluble in H_2SO_4 . Dissolved by $KHSO_3$.

Ign.—Readily volatilised without change of composition.

MgNH₄AsO₄.

Rem.—Usual precipitant, $MgCl_2$ in ammonia solution containing alcohol. Precipitate white, crystalline closely resembling $MgNH_4PO_4$.

Cond.—Solution alkaline with ammonia, containing a minimum amount of NH_4Cl and 25 to 30 per cent of alcohol. No sulphates or other compounds, partially or entirely insoluble in alcohol of this strength, should be present. The As must be in pentad form (a condition realised in solutions containing alkaline polysulphides).

Sol.—Dissolved by acids or on application of heat. Somewhat soluble in water and in NH_4Cl , an effect partly neutralised by presence of ammonia and alcohol, in which it is insoluble.

Contam.—Basic Mg salts, sulphates, and other salts partially or entirely insoluble in diluted alcohol.

Ign.—Partially volatilised if heated up quickly. By slow heating it is dried and finally altered to $Mg_2As_2O_7$, which is non-volatile. With C partly volatile. A convenient method of management consists in dissolving the washed precipitate through the filter by dilute HNO_3 into a weighed capsule, evaporating, igniting slowly and finally intensely.

Sb₂S₃.

Rem.—Usually precipitated by H_2S in acid solution, or by acidifying solutions of sulphantimonite.

On drying, the precipitate does not surrender all H_2O until the temperature is raised to $200^\circ C$, when it becomes black. This degree of heat is liable to char the paper when dried on a weighed filter.

By the action of oxidising agents (Br, HNO_3 , HgO , &c.) it is converted to Sb_2O_4 .

Cond.—Solution slightly acid and moderately dilute. An excess of H_2S causes a more rapid separation of the precipitate. If too acid or too concentrated the precipitation may be imperfect.

Sol.—Precipitate dissolved or prevented from forming by moderately concentrated acids, especially HCl. H_2SO_4 has much less effect. The preventive effect is increased with the temperature. Tartaric acid in the solution assists precipitation.

Dissolved by fixed alkalies or alkaline sulphides.

Scarcely soluble in ammonium carbonate or $KHSO_3$.

Somewhat soluble in $H_2C_2O_4$, but insoluble in it if boiled in presence of an excess of H_2S . (Separation from tin.)

Contam.—S usually accompanies the precipitate. To remove this the water is first displaced by alcohol, and the S dissolved out by CS_2 .

Ign.—Partially or entirely volatilised by ignition alone or by reducing agents. Mixed with 30 to 50 times its weight of HgO and ignited, it is converted to Sb_2O_4 , which is stable at the ordinary temperature of ignition. Frequently, however, it is converted to Sb_2O_3 by Br or HNO_3 before ignition.

H₁₀Sn₅O₁₅ or 5(H₂SnO₃).

Rem.—The above is called the "insoluble" form of hydrated stannic oxide, because not readily soluble. It is usually obtained by boiling slightly acid (HNO_3 or H_2SO_4) solutions containing the soluble form in partial

* From School of Mines Quarterly, xii., No. 4.

suspension, or by boiling weakly acid solutions (of stannic compounds) containing neutral alkaline salts (NH_4NO_3 , NaNO_3 , Na_2SO_4 , &c.). The presence of acetates assists the separation.

Cond.—HCl or chlorides should be small in amount, preferably entirely absent. Solution should be acid, tolerably dilute, and boiled for some time.

Sol.—The "soluble" form (obtained by neutralising stannic solutions with caustic or carbonated fixed alkalis) is readily soluble in excess of the alkali or in acids. The "insoluble" form is only soluble with difficulty in HCl or in caustic alkali, and practically insoluble in dilute HNO_3 or H_2SO_4 .

Contam.—As and Sb oxides, which should have been removed previously. In analyses of bronzes, &c., CuO removed by long digestion with dilute HNO_3 . SiO_2 , removable by treatment with HF and H_2SO_4 . Fe_2O_3 , removed by fusion with NaOH or Na_2CO_3 , and, after further treatment by well-known methods, separating the Fe_2O_3 , which is weighed and deducted. This operation is usually performed upon a weighed portion of the precipitate.

Ign.—Requires intense heating to remove all H_2O . Not easily reduced to (volatile) Sn by C, though such reduction is possible on igniting the precipitate. Volatilised as chloride by ignition with NH_4Cl . Otherwise not volatile at high temperatures.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

November 5th, 1891.

Mr. W. CROOKES, F.R.S., Vice-President, in the Chair.

Mr. J. Tudor Cundall was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. George James Allen, Ivy House, Bolton Road, Pendleton; George Alfred Ashcroft, 88, Alexandra Road, Manchester; Harold Alger, The Manor House, Stoke, Devonport; Edward Charles C. Baly, Bank of England; Thomas William Berry, Shireoaks, Worksop, Notts; Samuel Francis Burford, Eastleigh, Queen's Road, Leicester; John Bairstow, 32, Sealand Road, Chester; J. Treeby Barratt, Mostyn, North Wales; John Redman Bovell, Dodds, Barbados; John C. Chorley, Lodge Lane, Bewsey, Warrington; George Edward Cory, The Public School, Grahamstown, South Africa; Thomas Darling, 1, Palace Street E., Berwick-on-Tweed; Charles E. Eastick, Myrtle Bank, Leyton; Percy Elford, Christ Church, Oxford; Lionel William Fulcher, 37, Melford Road, Lordship Lane, S.E.; George German, Jun., Aseby-de-la-Zouch; Alfred Daniel Hall, Martyn Road, Guildford; Archibald Hall, 34, Bishopsgate Street; John Holliday, 7, Aglionby Street, Carlisle; John Walter Leather, 15, Bradgate Road, Catford, S.E.; Lionel Ludlow, 90, Walter Road, Swansea; John Willis Marshall, 10, Palatine Square, Burnley; Daniel McLaren, B.Sc., 30, Raleigh Street, Nottingham; Joseph Morris, Stamford Street, Mossley, near Manchester; William Naylor, 182, Newhampton Road, Wolverhampton; Thos. Neilson, 26, Harrington Road, Workington, Cumberland; Abhayacharan Sauyal, M.A., Muir Central College, Allahabad; Walter Thorp, 3, Melbourne Villas, Headingley, Leeds; A. W. Winterton, 6, Lindum Terrace, Rotherham; John Henry Wilson, 29, Radford Street, Coventry.

The following papers were read:—

59. "The Magnetic Rotatory Power of Solutions of Ammonium and Sodium Salts of some of the Fatty Acids." By W. H. PARKIN, Ph.D., F.R.S.

Ostwald, in his paper on magnetic rotation (*C. S. Trans.*, 1891, 198) has argued that the peculiar results obtained by the author in the case of solutions of acids and of ammonium salts, &c., are in accordance with the electrolytic dissociation hypothesis; and has suggested that, since salts formed from weak acids are as good conductors as those formed from strong ones, we may expect in this case, also, marked deviations from the calculated values. The same chemist, in his work on Solutions, considers that there can be no doubt that such salts as ammonium formate, &c., when in aqueous solution, would show molecular rotations which would not be the sums of the rotations of the components of the salts, as must (nearly) be the case if the view put forward by the author be correct, that such salts are almost entirely dissociated into acid and base. Experiments made with the object of throwing further light on the subject have afforded the following results:—

	Mols. Water to 1 mol. Salt.	Mol. Rot.	Average Mol. Rot.
Ammonium formate ..	3'00	3'363	
" " ..	8'78	3'394	
" " ..	10'00	3'333	3'363
" acetate ..	4'75	4'246	
" " ..	13'13	4'247	4'246
" propionate ..	2'86	5'255	
" " ..	10'26	5'263	5'259
Sodium formate ..	5'40	2'364	
" " ..	12'54	2'331	2'347
" acetate ..	11'23	3'281	3'281
" propionate ..	7'00	4'308	4'308
" butyrate ..	6'81	5'332	5'332

It will be seen that the rotatory powers of the ammonium salts do not vary with dilution; there can be little doubt that this is true also of the sodium salts, as sodium formate shows no difference on dilution. Comparing the experimental values obtained in the case of the ammonium salts with those afforded by the constituent acid and ammonia, the following results are obtained:—

CH_3O_2 ..	1'671	$\text{C}_2\text{H}_3\text{O}_2$..	2'525	$\text{C}_3\text{H}_5\text{O}_2$..	3'462
NH_3 ..	1'818		1'818		1'818
	3'489		4'343		5'280
Am. salt ..	3'363		4'246		5'259
Diff. ..	0'126		0'095		0'021

As might be expected, as reduction of rotatory power always attends combination, the values are slightly less in the case of the salts. The author points out that the reduction is very nearly the same as that which takes place in the formation of the corresponding ethereal salts, and as these salts are anhydrous the results may be held to justify the conclusion that the values obtained for ammonium salts in solution are practically those of the dry salts, and therefore that Ostwald's views are inapplicable. In the case of sodium salts it is more difficult to arrive at a conclusion, as the value of sodium is unknown, but it is shown that whatever influence water has on them it is to be supposed that it acts to the same extent on all the four salts examined.

60. "Note on the Action of Water Gas on Iron." By Sir H. E. ROSCOE and FRANK SCUDDER.

During some experiments which the authors have recently been making on the application of water gas for illuminating purposes by means of the well-known Fahnnehjelm system, it was occasionally observed that after the water gas had impinged on the comb for some hours a deposition of ferric oxide was formed on the magnesia rods, the result being that the illuminating power was considerably lowered.

It was at first suggested that the iron came from the particles of dust which were present in the atmosphere of the steel works where these experiments were being conducted. Further examination of the tips of the steatite

burners showed, however, that the deposit of ferric oxide was "coralloid," and that, therefore, it could not be produced from dust in the atmosphere, but was contained in the gas itself. In order to ascertain whether the iron was in a gaseous state or in the form of finely divided particles, the gas was filtered through several tight plugs of cotton wool; but as a similar deposit was observed after four or five hours, it was concluded that the water gas contained a volatile iron compound.

These facts, although interesting, only showed that the quantity of the volatile iron compound was extremely small, apparently precluding all hope of extracting sufficient of the material for analysis. Nevertheless the occurrence of iron, even in these minute quantities, was a most serious bar to the technical application of water gas as an illuminant, and the question of its origin as well as its removal became of practical interest.

In the course of experiments made for another purpose, water gas was compressed in steel cylinders to a pressure of 8 atmospheres, and on burning the gas immediately after compression no visible alteration in the colour of the flame or in the amount of iron contained in the gas was observable; but after the compressed gas had remained in the cylinders for about a month, it was found that when it was burned from a steatite burner the flame was highly luminous, and instantly deposited on the Fahnehjelm comb a yellowish red coating of ferric oxide: proving that a much larger quantity of iron was contained in the gas which had been kept than in the original compressed gas.

On passing a small quantity of the gas through a piece of combustion tubing heated externally by a Bunsen burner, a large deep black mirror was rapidly formed, which proved on analysis to be metallic iron, free from carbon, arsenic, and antimony.

The flame, however, still remained strongly luminous, particles of metallic iron burning brightly in it, whilst either a black mirror of metal or one of ferric oxide was deposited on a porcelain plate held above it according to the position in which the plate was held. On inserting a plug of cotton wool between the heated portion of the tube and the burner, the flame instantly became non-luminous, and in a few seconds the cotton wool nearest to the heated part of the tube became black; in a short time the whole plug was deeply stained with finely divided metal. Hence it was evident that under a pressure of 8 atmospheres the carbonic oxide contained in water gas (about 39 per cent of its bulk) slowly attacked metallic iron at the ordinary atmospheric temperature.

In a preliminary determination in which about 30 litres of gas was burned in half an hour, the weight of the metallic iron deposited as a mirror amounted to 0.0322 grm., whilst that found on the plug of cotton wool was 0.0406 grm., a total of 0.0728 grm. of iron, equal to 2.4 m.grms. per litre.

Although the compound, which is, doubtless, the iron carbonyl of Mond and Quincke, is only present in this small quantity, the authors have found that it can readily be liquefied if the gas be passed through a cotton-plugged tube and then led into a U-tube surrounded by a mixture of salt and ice: a few drops of turbid liquid thus deposited became clear on treatment with a little hydrochloric acid, and on adding potassium ferrocyanide a deep blue colour was obtained.

The authors hope, before long, to communicate more detailed information as to the causes of the occasional occurrence of the volatile iron compound in water gas, and as to its nature. The action of water gas on other metals will also receive their attention.

DISCUSSION.

The CHAIRMAN referred to the fact that at the recent British Association Meeting at Cardiff Mr. Mond had exhibited specimens not only of liquid iron carbonyl, but also of a solid compound of iron with carbonic oxide.

Prof. RAMSAY stated that he had found that the com-

pound of nickel with carbonic oxide was formed in the cold, the action frequently going on for days. He subsequently added, in reply to a question by Mr. Groves whether dry pure carbonic oxide acted on iron, that in the case of nickel, the gas acted equally well when dried by phosphoric anhydride.

Sir Henry Roscoe, in the course of his account, had mentioned that ordinary coal gas contained traces of iron, pointing out that this was the cause of the stain observed on steatite burners. Referring to this point, Dr. THORNE mentioned that he had recently had occasion to detect iron in compressed coal gas, which was now frequently used for the production of the limelight. In using such gas it was sometimes noticed that the lime cylinder acquired a brown deposit, and it was owing to this circumstance that he was led to examine the gas.

61. "*The Dissociation of Liquid Nitrogen Peroxide.*" By J. TUDOR CUNDALL, B.Sc., Lecturer on Chemistry in the Edinburgh Academy.

The author has determined, by colorimetric methods, the relative amount of NO_2 formed in liquid nitrogen peroxide (i.) by dilution with chloroform, (ii.) by rise of temperature. He has also ascertained the absolute amount of dioxide by comparing the colour of the liquid solution with that of the gas containing a known amount of nitrogen dioxide. The results go to show that, on dilution, (i.) dissociation takes place very slowly at first, but more rapidly when less than 5 per cent of the peroxide is taken; (ii.) that solutions of the peroxide dissociate more rapidly than the pure liquid on rise of temperature. In the most dissociated solution yet examined, viz., one to which had been added 1.44 per cent of peroxide by vol. at 25°C ., not more than 1.22 per cent of NO_2 was present.

DISCUSSION.

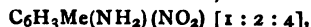
Prof. RAMSAY pointed out that the fact established by Mr. Cundall, that nitrogen peroxide was dissociated to but a slight extent on dilution unless the solution were very dilute, was a confirmation of the result which he had obtained on determining the molecular weight of the peroxide by Raoult's method.

Prof. THORPE suggested that the rate of dissociation might possibly be ascertained by determining the relative densities of solutions of nitrogen peroxide at different temperatures.

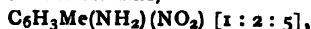
Mr. CUNDALL thought that the variation was too slight to permit of the application of such a method.

62. "*Ortho- and Para-nitro-orthotoluidine.*" By ARTHUR G. GREEN and THOR. A. LAWSON, Ph.D.

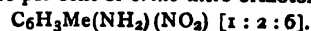
It has been shown by Nörling and Collin (*Ber.*, 1884, 265) that when orthotoluidine sulphate is nitrated at a low temperature in presence of a large excess of sulphuric acid, *para*-nitro-orthotoluidine,—



results. This isomer appears to have been considered to be the only product of the interaction under these conditions, but the authors have found that this is by no means the case, for besides the *para*-nitro-orthotoluidine (about 75 per cent) there is formed about 3 or 4 per cent of *meta*-nitro-orthotoluidine,—



and about 20 per cent of *ortho*-nitro-orthotoluidine,—



The latter, which up to the present has only been obtained by reduction of the consecutive dinitrotoluenes, like *para*-nitro-orthotoluidine, has the NH_2 and NO_2 groups relatively in the *meta*-position, and hence the simultaneous formation of these two isomers (the 1:2:6 and the 1:2:4) by nitration of orthotoluidine in presence of sulphuric acid might have been theoretically expected.

The separation of the *ortho*-nitro-orthotoluidine from the mixture is effected by taking advantage of the greater solubility of this isomer in slightly warm water.

Having at their disposal considerable quantities of the ortho- and para-nitro-orthotoluidine, the authors have made a comparison of these two isomers and of their products of reduction and other derivatives, which is summarised in the foregoing table.

63. "Researches on the Gums of the Arabin Group. Part II. Geddac Acids. Gedda Gums; the Dextrorotatory Varieties." By C. O'SULLIVAN.

The Gedda gums described consist of the calcium, magnesium, and potassium salts of gum acids, the calcium salt predominating, together with more or less nitrogenous matter, which is probably in some way combined with a true gum acid.

They dissolve easily in water, forming a yellow or reddish syrup, neutral to test-paper, which is dextrorotatory.

If the solution be acidified and dialysed for some time, the whole of the ash may be separated, and if alcohol be added carefully to the dialysed liquid, a powdery precipitate first separates which contains the whole of the nitrogenous bodies and some gum acid; on allowing the precipitate to deposit, and then decanting the clear supernatant liquid, and adding alcohol, a syrupy precipitate is obtained, consisting of a mixture of the gum acids present in the natural gum. By repeatedly fractionating the aqueous solution of these gum acids by alcohol, they were separated from one another and obtained in a pure state.

The gum acids contained in any one sample of gum bear a very simple relation to one another, and they are also intimately related to the gum acids contained in other samples. These relationships are indicated in Table I.

Of these gum acids, those having the highest molecular weight are most soluble in dilute alcohol.

The gum acid of gum arabic is similarly constituted, being, in fact, di-arabinantetragalactanarabic acid,—

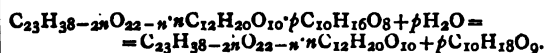


and the acids present in the third sample of Gedda gum described are similarly constituted, geddic and arabic acids being isomeric.

The composition and partial constitution of any one of the gum acids which have been as yet examined may be expressed by the general formula—



When a solution containing 2 per cent H_2SO_4 of any one of these gum acids is heated at 80–100° C. for ten to thirty minutes, the gum acid is hydrolysed, yielding arabinon and a gum acid of lower molecular weight, the whole of the arabinon residue indicated in the general formula being liberated. The change may be expressed as follows:—



The greater portion of the arabinon thus produced is hydrolysed to arabinose, $C_{10}H_{18}O_9 + H_2O = 2C_5H_{10}O_5$.

It is possible by carefully restraining the hydrolytic action to obtain gum acids which still contain the arabinon residue, but, under the conditions given, practically the whole of the arabinon obtainable is produced.

The gum acids thus produced are separated from the sugars by treatment with alcohol; they very closely resemble the gum acids existing in the natural gums, but are less optically active and less soluble in weak alcohol.

As is evident from the formulæ given above, any one of the gum acids contained in a given sample of gum, when thus hydrolysed, yields the same gum acid; and the acids obtained from the natural acids of different samples are closely related together. This is indicated in Table II.

It is noteworthy that these acids bear a relation to one another similar to that of the different acids contained in any one sample of the natural gums. The most marked point of difference between these gum acids and those

1 : 2 : 6	M. p. 91.5° (Bentzen (G. and L.). Fine, light- yellow needles; not sweet.	M. p. 142 to 143° (Uhlmann). 143 to 144° (G. and L.). Compact, yellow needles; slightly sweet.	M. p. 103.5° (Uhlmann), 103° (G. and L.). Prisms.	M. p. 202 to 203° (G. and L.). Sublimes in very light flocks.	M. p. 149° (G. and L.). Pale-yellow plates.	M. p. 307° (G. and L.). Small, white, flat needles.	M. p. 175° (G. and L.). Orange plates.	M. p. 340° (G. and L.). Small, yellow needles.	M. p. 370° (G. and L.). Long, white needles.	M. p. 161° (G. and L.). White, prismatic needles.
1 : 2 : 4	M. p. 107° (Nöling and Collin). 107.5° Fine, yellow- ish needles; very sweet taste.	M. p. 107 to 108° (Nöling and Collin). Fine, yellow- ish needles; very sweet taste.	M. p. 99° Prismatic crystals.	M. p. 221° (Tiemann). 224° (Laden- burg). Does not sublime in flocks.	M. p. 168° (Limpficht), (G. and L.). Yellow needles or orange prisms.	M. p. 290° (G. and L.). Small, white needles.	M. p. 197° (Limpficht), 203° (G. and L.). Orange, prismatic needles.	M. p. 300° (G. and L.). Small, yellow needles.	M. p. 65.5° (Wachen- dorf), 68° (G. and L.). Long, white needles.	M. p. 136 to 137° (Wachen- dorf).
	CH ₃ NH ₂ NO ₂	CH ₃ OH NO ₂	CH ₃ NH ₂ NH ₂	CH ₃ NHAc NHAc	CH ₃ NH ₂ N ₂ O	CH ₃ NHAc N ₂ O	CH ₃ NH ₂ N ₂	CH ₃ NHAc N ₂	CH ₃ Cl NO ₂	CO ₂ H Cl NO ₂

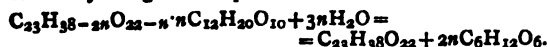
TABLE I.

Name.	Formula.	[α] _D .	P.c. BaO in Ba salt.
Gedda gum I.			
Tetrarabinantrigalaçangeddic acid	$4C_{10}H_{16}O_8 \cdot 3C_{12}H_{20}O_{10} \cdot C_{23}H_{32}O_{19}$	+ 59°	5.59
Triarabinantrigalaçangeddic acid	$3C_{10}H_{16}O_8 \cdot 3C_{12}H_{20}O_{10} \cdot C_{23}H_{32}O_{19}$	+ 49°	6.05
Diabinantrigalaçangeddic acid	$2C_{10}H_{16}O_8 \cdot 3C_{12}H_{20}O_{10} \cdot C_{23}H_{32}O_{19}$	+ 43°	6.75
Monarabinantrigalaçangeddic acid	$C_{10}H_{16}O_8 \cdot 3C_{12}H_{20}O_{10} \cdot C_{23}H_{32}O_{19}$	+ 37°	7.65
Gedda gum II.			
Nonarabinantrigalaçangeddic acid	$9C_{10}H_{16}O_8 \cdot 4C_{12}H_{20}O_{10} \cdot C_{23}H_{32}O_{18}$	+ 110°	3.46
Heptarabinantrigalaçangeddic acid	$7C_{10}H_{16}O_8 \cdot 4C_{12}H_{20}O_{10} \cdot C_{23}H_{32}O_{18}$	+ 100°	3.93
Pentarabinantrigalaçangeddic acid	$5C_{10}H_{16}O_8 \cdot 4C_{12}H_{20}O_{10} \cdot C_{23}H_{32}O_{18}$	+ 90°	4.55
Triarabinantrigalaçangeddic acid	$3C_{10}H_{16}O_8 \cdot 4C_{12}H_{20}O_{10} \cdot C_{23}H_{32}O_{18}$	+ 80°	5.40

TABLE II.

Obtained by the action of sulphuric acid on the gum acids contained in—	Name.	Formula.	[α] _D .	P.c. BaO in Ba salt.
Gedda gum III.	Pentagalaçangeddic acid.	$C_{23}H_{32}O_{17} \cdot 5C_{12}H_{20}O_{10}$	+ 30°	6.51
Gedda gum II.	Tetragalaçangeddic acid.	$C_{23}H_{30}O_{18} \cdot 4C_{12}H_{20}O_{10}$	+ 22°	7.49
Gum arabic.				
Gedda gum I.	Trigalaçangeddic acid.	$C_{23}H_{32}O_{19} \cdot 3C_{12}H_{20}O_{10}$	+ 20°	8.81

present in the natural gum is their behaviour when heated with a 2 per cent solution of sulphuric acid; they offer great resistance to the hydrolytic action of this acid, but are slowly broken down by several hours' digestion, the galaçan residue being removed, and acids of successively lower weight being formed; the lowest stage is represented by the general equation—



The properties of the compound $C_{23}H_{38}O_{22}$ have not yet been very accurately determined, the difficulty being to obtain a sufficient quantity.

This gum acid and the others obtained after the partial hydrolysis of the galaçan residue can only be precipitated from their concentrated aqueous solutions by very strong alcohol; they are dialysable, and strongly acid.

Those obtained from Gedda gum are highly dextro-rotatory, whilst those from gum arabic, although otherwise identical, are inactive.

64. "Some Compounds of the Oxides of Silver and Lead." By EMILY ASTON, B.Sc.

The author finds that on following the directions given by Wöhler (*Pogg. Ann.*, 1837, xli., 344) for the preparation of the compound $Ag_2O, 2PbO$, the product varies in composition, the highest percentage of silver obtainable being 49.01, whereas the amount required for Wöhler's compound is 34.23.

When a mixture of lead and silver hydroxides is allowed to stand in presence of caustic soda, a change of colour occurs, and after repeated extraction with caustic soda, a substance is left having a composition nearly that required by the formula $2Ag_2O, PbO$. A product of similar composition is obtained by precipitating the mixed nitrates of lead and silver, and exhaustively extracting with caustic soda.

Attempts to prepare compounds of lead oxide with the oxides of barium, strontium, sodium, and potassium were unsuccessful.

65. "The Electrolysis of Potassium Acetate Solutions." By T. S. MURRAY, D.Sc.

On electrolysing a very dilute aqueous solution of potassium acetate, only hydrogen and oxygen are evolved; if the solution be a concentrated one, the gaseous product is a mixture of ethane, hydrogen, oxygen, methyl acetate (trace), and carbon dioxide: a portion of the carbon dioxide arises from oxidation of some part of the electrolyte, or product of the electrolysis.

The author has investigated the influence of concentration of solution, strength of current, size of electrodes, temperature, &c., on the course of the electrolysis. He

proves the absence from the gas of acetone, methyl oxide, ethylene, or any unsaturated hydrocarbon.

On diluting the solution of acetate, the amount of ethane produced decreases, at first very slowly, but finally with great rapidity. For instance:—

Per Cent.

A 60 solution gave ethane = 80.0 (hydrogen = 100).

" 11.77 " " " = 73.5

" 1.84 " " " = 50.8

" 0.50 " " " = 0.003

Reducing the current has a similar influence. With rise of temperature, the ethane diminishes in quantity more rapidly the higher the temperature, and ceases to be formed at about 100° C.

In contradiction to Jahn, he finds that the employment of a large anode reduces the yield of ethane, the largest yield being obtained by the use of a very small anode; variations in the cathode do not influence the electrolysis. The presence of acetic acid, or of alkali, even in small quantity, reduces the yield of ethane.

The oxidation of the electrolyte to carbon dioxide, which proceeds simultaneously with the formation of ethane, is affected very differently by changes in the several conditions. Thus for a given yield of ethane = 25 say (hydrogen = 100), the corresponding oxidations produced are by change of current, 96; by varying size of anode, 68; by varying concentration, 60; by varying the temperature, 50; possible oxidation being taken as 100. With a yield of ethane about 75, no matter how it is obtained, the oxidation is always about the same, namely, 94.

The results of the investigation are illustrated by a series of curves. The author believes that he has demonstrated that the ethane is formed, not by a partial oxidation of acetic acid, as Bourgoin, Jahn, and Bunge believe, but that it results from a simple interaction of the acetions ($CH_3 \cdot COO$). He finds that the yields of ethane obtained from equivalent solutions of potassium, sodium, and calcium acetates are equal.

66. "A New Method of Preparing β-Dinaphthylene Oxide and the Constitution of its Tetrasulphonic Acid." By W. R. HODGKINSON and L. LIMPACH.

The method in question is to heat the sodium salt of 2:3'-β-naphtholsulphonic acid (Schaefer's acid) to low redness; the distillate also contains β-naphthol and β-dinaphthyl ether: the former having been extracted by alkali, the residue is dissolved in acetic acid; as the solution cools the oxide separates as a yellow, fluorescent substance, and when recrystallised forms rhombic plates melting at 153°. Its picrate crystallises from alcohol in

dark red needles melting at 134. It is easily converted into a tetrasulphonic acid.

The same tetrasulphonic acid is formed by the continued action of sulphuric acid on β -naphthol.

CORRESPONDENCE.

BEEF FAT.

To the Editor of the Chemical News.

SIR,—In his letter (CHEMICAL NEWS, vol. lxi., p. 224) Mr. A. H. Allen writes "For tallow read beef fat, which is practically synonymous, and my statement is absolutely correct." From that statement I totally dissent, and now deny ever having even mentioned caustic potash (KHO); for caustic potash read caustic soda (which, according to Mr. Allen, is practically synonymous), and my results are absolutely correct,—results which I am perfectly satisfied with, the accuracy of which no unprejudiced person would gainsay. I have, however, re-determined the fatty acids in the exact sample with the following results—94.42 and 94.48 per cent, results which agree remarkably well with the original estimations, which were as follows:—Fatty acids, 94.24 and 94.52 per cent; and the normal soda consumed by 2.5 grms. 10.54 and 10.57 c.c.

If one calculates the glyceryl (C_3H_5) from the amount of KHO consumed, we obtain—

C_3H_5	5.40
Fatty acids .. —	94.38
	99.78

Results which were actually obtained from pure beef fat, even though ridiculed by your correspondent. Since the publication of the original results I have continued my investigation of the constitution of butter-fat, and am now in a position to announce that I have been enabled to separate butter-fat into two distinct glycerides (by means of a particular solvent used in a proper manner), the triglyceride of Wanklyn's aldi-palmitic acid, and another glyceride containing a new fatty acid with an iodine absorption considerably less than half that of oleic acid.

The whole results of my research in this direction will shortly be published, so in the meantime Mr. Allen will perhaps kindly explain the exact meaning of his most unaccountable and uncalled for criticism.—I am, &c.,

WILLIAM JOHNSTONE.

13, Fish Street Hill,
November 20, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 19, November 9, 1891.

Study of the Boron Phosphorides.—Henri Moissan.—Boron triiodide, BI_3 , yields in the cold, in contact with a sulphocarbonic solution of phosphorus, a phosphoride of the formula PBI_2 . This compound, which may be obtained in a crystalline state by volatilisation, yields when reduced in hydrogen the phosphoride PBI , and ultimately the phosphide PB . If it is still heated in hydrogen a part of the phosphorus escapes as a vapour, and there remains a new phosphide of the formula P_3B_5 .

Existence of Acid or Basic Salts of the Monobasic Acids in very Dilute Liquids.—D. Berthelot.—

The author has shown that the addition of an excess of alkali to a neutral salt formed by the same alkali appears always to exert a slight chemical action, which is manifested only for the first portions of alkali, the succeeding portions having no particular effect. This phenomenon occurs as well with feeble organic acids, such as the acetic, as with the strong mineral acids. Hence it seems to result that even in very dilute liquids there is a tendency to the formation of a basic salt in small quantities, whilst the formation of an acid salt is less marked in solutions of the same dilution.

The Formation of Saline Hydrates at High Temperatures.—G. Rousseau.—The author's results seem to establish the formation of saline hydrates at high temperatures. He believes that it is possible to add new members to this family of compounds. Except manganese all the metals capable of giving rise to these hydrates belong to the eighth group of the periodic classification. From analogy it is legitimate to admit that the other members of this group may yield hydrates of the same order. The author purposes verifying this conjecture for the aurates and the osmites. Ruthenium, which was formerly placed in the eighth group, should be transferred to the seventh, following manganese according to the modified atomic weight assigned to it by the determinations of Joly. But the parallelism of the oxides of manganese and ruthenium enables us to foresee the existence of hydrated sodium and potassium ruthenites comparable to the alkaline manganites.

A Double Copper and Lithium Chloride.—A. Chassevant.—The author assigns to this compound the formula $2CuCl \cdot LiCl + 5HO$. The salt does not dissolve in water without decomposition. If we add to it small quantities of water we obtain a green solution which quickly becomes blue. This colouration indicates the dissociation of the double salt in contact with water; the copper chloride and the lithium chloride are separated in the liquid. If we take as solvent a concentrated solution of lithium chloride the double chloride dissolves in it without decomposition, giving a reddish brown solution from which it can be re-crystallised.

Researches on Digitaleine.—J. Houdan.—The composition of digitaleine is $C_{62}H_{52}O_{24}$. Its most characteristic property is the following:—If we add amyl alcohol to an aqueous solution of digitaleine there is rapidly produced an abundant crystallisation. Digitaleine crystallised in ordinary alcohol loses its water and its alcohol at 110° . It dissolves slowly in cold water, but rapidly in boiling water. In absolute alcohol it is very sparingly soluble. Chloroform, ether, and ligroine only take up traces. It deflects the plane of polarisation to the left. It dissolves in hydrochloric acid without becoming coloured, but if the solution is heated it turns to a reddish violet with a slight green fluorescence. Dilute acids split it up into two glucosides without liberation of glucose.

On the Isocinchonines.—E. Jungfleisch and E. Léger.—A question of priority as against Herr Heese.

Determination of Fatty Matter in Dairy Products.

—Lezé and Allard.—(See p. 265).

Ptomaines Extracted from Urine in some Infectious Diseases.—A. B. Griffiths.—The author has isolated the ptomaine of scarlet fever, $C_7H_{12}NO_4$, a white crystalline substance soluble in water and having a feebly alkaline reaction. It forms a crystalline hydrochlorate and a chloraurate. It gives a yellowish white precipitate with the phosphomolybdic acid, a white with the phosphotungstic, and a yellow with picric acid. The ptomaine of diphtheria, $C_{14}H_{17}N_2O_6$, is also white and crystalline. It gives a hydrochlorate and a chloraurate. It is precipitated of a yellow colour by tannic acid and picric acid, white by phosphomolybdic, and brown by Nessler's reagent. A very poisonous ptomaine was obtained from a patient suffering from congestion of the kidneys, the

parotid" and submaxillary glands. Its composition is $C_6H_{12}N_4O_3$. This base is transformed into creatine, then into methylguanidine. These three ptomaines are not found in normal urine.

Journal für Praktische Chemie.
New Series, Vol. xlv., Parts 16 and 17.

Action of Hydrazine Hydrate upon Monoketones and Orthodiketones.—Th. Curtius and K. Thun.—Hydrazine hydrate acts upon the ordinary monoketones in a two-fold manner. If the ketones are introduced into an excess of hydrazine hydrate there are formed secondary nonsymmetric hydrazines which are very unstable and easily pass even in the cold into the very stable form of the azines, whilst hydrazine is split off. The same azines are obtained in a direct manner if the calculated quantity of hydrazine hydrate is added to 2 mols. of ketone. The authors have caused hydrazine hydrate to react upon acetone, methylethylketone, methylpropylketone, methylhexylketone, diethylketone, and acetophenone. In diketones on the action of hydrazine hydrate the keto-oxygen atoms are successively replaced by the hydrazo-group (N_2H_2).

Action of Hydrazine Hydrate upon Isatine and the Phenols.—Th. Curtius and K. Thun.—Isatine in contact with hydrazine hydrate behaves similarly to the orthodiketones. Equimolecular mixtures of phenol or hydroquinone and hydrazine hydrate yield, even when heated in sealed tubes to 130° , only the diammonium salts of these bodies.

Action of Hydrazine Hydrate upon Benzophenone.—Th. Curtius and F. Rautenberg.—An account of diphenylmethylenhydrazine, its behaviour with acids, diphenylmethylenhydrazine hydrochlorate, the acetyl derivatives of diphenylmethylenhydrazine, the decomposition of bisdiphenylazimethylen on boiling with acids; the behaviour of diphenylmethylenhydrazine when heated alone or with diphenylmethylenetetrazone, the action of halogens and haloid hydracids upon the tetrazo-compound, the action of aldehyds and ketones upon diphenylmethylenhydrazine, diphenylmethylenbenzolzazine, diphenylmethylenecinnamalazine; the behaviour of chloral with diphenylmethylenhydrazine, diphenyldimethylazimethylen, diphenylmethylcinnamalazimethylen; the reaction of diphenylmethylenhydrazine and methylpropylketone and bisdiphenylazimethylen.

Phenomena of Isomerization of the Non-Saturated Hydrocarbons.—(Part IV.)—Al. Faworsky.—Monosubstituted acetylenhydrocarbons react on heating with alcoholic alkali. The first membrane of the series of the monosubstituted hydrocarbons, allylen, combines under these conditions the elements of the alcohol, and yields ethylisopropenylether; its higher homologues undergo an isomeric transformation. Monosubstituted acetylenes with primary alkyl radicles are isomerised to bisubstituted acetylenes. The isomerisation is complete at 140° — 170° . Monosubstituted acetylenes with secondary radicles under the influence of alcoholic alkali are isomerised to non-symmetric bisubstituted allenes. With tertiary radicles the monosubstituted acetylenes do not react if heated with alcoholic alkali.

Researches from the Laboratory of the University of Freiburg.—These consist of a memoir by P. Heermann and N. Teclu on the nitroderivatives of α -naphtholethylether.

Characterisation of Flame.—N. Teclu.—The experiments described and illustrated in six figures show that a coal-gas flame by the action of atmospheric oxygen can be split up into two flames, one of which continues quietly burning at its original place, whilst the other travels downwards.

Optical Determination of the Quantity of Albumen in Urine.—H. O. G. Ellinger.—Already inserted.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Thermo-Chemistry.—A correspondent wishes for information as to where he can find thermo-chemical facts of elements (metals) not thermo-chemically known before 1886.

Gold-Aluminium.—Can any of your readers give me any information respecting the gold-aluminium alloy ($AuAl_3$) discovered by Prof. Roberts-Austen, or tell me where such can be obtained?—A.B.

MEETINGS FOR THE WEEK.

MONDAY, 30th.—Society of Arts, 8. "The Pigments and Vehicles of the Old Masters," by A. P. Laurie, M.A.

WEDNESDAY, Dec. 2nd.—Society of Arts, 8. "Secondary Batteries," by G. H. Robertson, F.C.S.

THURSDAY, 3rd.—Chemical, 8. "Phosphor Oxide (Part II.)," by Prof. Thorpe, F.R.S., and A. E. Tutton. "On Frangulin," (Part II.), by Prof. Thorpe and Dr. A. K. Miller. "The Structure and Character of Flames," by A. Smithells and H. Tingle. "The Composition of Cooked Vegetables," by Miss K. I. Williams. "On the Occurrence of a Hydriatic Alkaloid in Lettuce," by T. S. Dymond. "On Some Metallic Hydrosulphides," by S. E. Linder and H. Picton. "On the Physical Constitution of some Solutions of Insoluble Sulphides," by Harold Picton. "Solution and Pseudo-Solution," by H. Picton and S. E. Linder. Ballot for the Election of Fellows.

FRIDAY, 4th.—Physical. "On a Permanent Magnetic Field," by Mr. W. Hibbert. "Note on the Production of Rotatory Currents," by Prof. Ayrton, F.R.S.

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AND
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THE CHEMICAL NEWS.

VOL. LXIV., No. 1671.

VACUUM SPECTRO-PHOTOGRAPHY.*

By Prof. V. SCHUMANN.

By means of a new vacuum spectro-photograph which I have personally constructed during the last twelve months, I have found it possible to resolve into separate lines the region of the hydrogen spectrum discovered last year (see *CHEMICAL NEWS*, vol. lxiii., p. 299, Dec. 29, 1890), situate beyond the wave-length 1820, and, in addition, to photograph a more refrangible region which likewise displays a considerable wealth of rays. The number of the lines of the resolved groups is far greater than could be expected from my last year's photographs. For instance, in one of these groups, the length of which does not exceed 11 m.m., I count more than 90 sharply defined lines. The width of my slit had to be selected not above 0.004 m.m. The success of such delicate proofs depend also on an exceptionally fine texture of the sensitive plate.

NOTE ON ESTIMATION OF PHOSPHORIC ACID IN SLAGS.

By VINCENT EDWARDS, F.C.S.

HAVING to analyse some samples of slag which contained a considerable quantity of phosphoric acid, and finding they obstinately resisted treatment with aqua regia, it occurred to me that boiling with concentrated sulphuric acid might be effectual. This I carried out in a small flask, such as is used for Kjeldahl's process, adding a globule of mercury at the same time. I took about 0.5 grm. of the substance, which contained much silica and carbon, and boiled till almost white; this took a little over an hour. On cooling I diluted to 250 c.c., filtered off 100 c.c., and precipitated the P_2O_5 by direct addition of citro-magnesian solution and ammonia; after standing collected the precipitate, dissolved in dilute nitric acid, and estimated by uranium solution, it being impossible to weigh as the precipitate contained a white substance insoluble in nitric acid, most likely silica; this might, however, be removed by evaporation.

The process appears satisfactory, and gave 4.5 per cent P_2O_5 more than by treatment in the usual way with HCl and HNO_3 . It is quite as simple as by any fusion method, and appears to be a means by which many complex substances which contain phosphoric acid might be dissolved and determined.

Lawes' Chemical Works, Barking,
November 12, 1891.

ON CHEMISM IN LIVING PROTOPLASM.

By Prof. W. PREYER and G. WENDT (of Berlin).

SINCE the memorable synthesis of urea, by which Woebler in 1828 gave a new direction to bio-chemistry, so many complicated products of animal and vegetable metabolism,—from formic acid to alizarine, salicine, coniline, and neurine,—have been obtained artificially, the somewhat premature conclusion that the belief in an especial vital force had been rendered perfectly untenable

has constantly gained more adherents. The opponent of vitalism inferred that in living organisms the same powers must exclusively prevail as in inorganic nature, seeing that a series of chemical compounds, hitherto known only as the products of vital processes, had now been obtained in the laboratory.

Important as this assumption has been and will doubtless remain, it derives little support from synthetic chemistry. For however many products of the anaplastic or—which is less surprising—of the kataplastic metabolism of animals and plants are artificially put together from their elements by all manner of round-about methods, this is merely a fresh proof that these substances may be obtained by another process besides the one which the vegetal or animal organism uses in their production.

It is a fact that the chemist in his syntheses conducts a totally different process from the organism. Why, therefore, may not an especial energy be exerted in the organism, the so-called vital force? This question is raised by many to-day as it was sixty years ago. Quite recently at the opening of the British Association in Manchester, Roscoe said, after a decided rejection of the vitalistic hypothesis:—"We might raise the question whether any limit has been set to this synthetic power of the chemist? . . . Though the danger of dogmatising on the progress of science has already been seen in too many cases, we cannot help feeling that the chemist has for the present no prospect of breaking down the barrier which exists between the organised and the non-organised world."

Chemistry, as such without calling other facts into play, has certainly hitherto banished an especial vital power into the realm of fable. But if it should happen—and its early occurrence is important—it must be demonstrated that the chemical processes in the vegetal and animal organism must be capable of explanation by the existing natural laws, or by them and possibly by natural laws yet to be discovered and in harmony with them, and that in consequence some of the peculiar physiological reactions and syntheses can be elicited outside of the living organism exactly as within it.

This problem is capable of solution. But we must first apprehend what belongs to the performance of the ordinary chemical reaction; then which of these conditions are wanting or are modified in the chemical transformations in the organism, or if any novel conditions appear. If these differences are clearly shown, then such modified conditions for a chemical reaction can be produced artificially at pleasure; hence there would arise a bio-chemistry very different from and far more manifold than the chemistry of the day.

It may here be premised that such modified conditions of reaction really exist in the living cell, and that even in chemical manufactures "organism-reactions," accidentally discovered in practice, find their application. In such cases modern chemistry, when questioned concerning their origin, is accustomed to content itself with the phrase,—“not perfectly explicable.”

A considerable number of misty conceptions, such as “katalysis,” “power of contact,” “ferment,” “allotropy,” &c., cannot hide the imperfections of such poor attempts at explanation, as they are recognised by every competent and reflective observer.

For a chemical reaction to take place a relatively considerable number of conditions must be fulfilled. To ascertain these we ask what occurs without exception in every chemical reaction; we then exclude strictly whatever is not to be observed in every case.

We then observe that whatever can always be shown in every chemical reaction is indispensable for the occurrence of such reaction, or is a necessary concomitant phenomenon.

Those natural processes which we call chemical reactions must be distinguished from all others by something in a genetic respect, which characterises them as chemical processes, and which must not be wanting if they are to

* Extracts from a Letter from the Author to W. Crookes.

retain this character. This something must be that which always belongs to all chemical reactions.

Now it is a common character of all chemical reactions in the customary sense of the word occurring on the earth's surface that:—

1. Different materials come in direct contact.
2. Water or some other solvent must be present.
3. There arise electric currents.
4. Changes of volume and of
5. Thermic energy occur.
6. An action of mass is present.

In the text-books the chemical reaction, the foundation of chemistry, as such is scantily or not at all discussed. The metaphysical enquiry as to the ultimate ground throws the more proximate question into the shade. The six unconditional requirements of all chemical reactions are here collated probably for the first time.

It must be asked whether they are always to be found accompanying the chemism of organised matter. As the three fundamental functions of protoplasm, that ground-floor of all telluric life, we recognise:—(a) Change of matter; (b) change of energy; (c) change of form: b and c are impossible without a, and a consists of assimilation and dissimilation.

(To be continued).

THE BEHAVIOUR OF AZOIMIDE WITH LIVING ORGANISMS.*

By O. LOEW.

NITRONYDRIC acid or azoimide,—



discovered by Th. Curtius in the past year, and made known by his laborious and dangerous researches, is not merely of profound chemical importance, but excites a physiological interest. Can the salts of this remarkable acid, like the nitrates and nitriles, serve as a source of nitrogen for the nutriment of vegetable cells? If not, are these salts indifferent or poisonous? If poisonous, wherefore?

Having been put in possession of some sodium-azoimide by the great kindness of Prof. Curtius, I resolved to take these questions in hand.

1. Experiments with Phanerogams.

A culture solution was made up with magnesium sulphate and potassium monophosphate, 0.2 per thousand each; potassium chloride and calcium chloride, 0.1 per thousand each; and a trace of ferrous sulphate. To this liquid there was added 0.2 per thousand of sodium-azoimide; and to a second portion, instead of the last-mentioned substance, an equal quantity of ammonium sulphate. In each solution there were placed three barley seedlings of 3 to 3.5 c.m. in length. The next day a great difference was visible; the ammonia plants had grown distinctly, and measured on the third day respectively 10, 10.3, and 10.7 c.m. The azoimide plants had scarcely grown at all, and measured 3.1, 3.6, and 3.9 c.m. In the length of the roots there appeared an equally striking difference. On the fourth day yellow spots appeared on the leaves of the azoimide plants; and on the fifth day from the commencement of the experiment the plants had faded, and were dying in all parts. The ammonia plants meantime developed in the normal manner. Even three seedlings which had been placed for comparison in well-water, without the addition of any nutrient salts, remained healthy, and grew for some time. Hence sodium azoimide had evidently exerted a poisonous action. A poisonous action was also observed in lupin

seedlings, as the growth of the roots came to a close after the first day.

Leaves of *Valisneria spiralis*, after remaining for three days in the above solution of azoimide salt, had lost their vital turgescence, displayed no plasmatic currents, and the cells were dead. In the check solution, which contained nitrogen in the form of ammonium sulphate, the leaves remained alive and the cells displayed lively plasmatic currents. Leaves of the hazel-nut plant, placed in the solution of sodium-azoamide, showed brown spots after three days.

2. Experiments on Alga.

A number of threads of *Spirogyra*, *Zygnema*, *Mesocarpus*, *Oscillaria*, also cells of Desmidiaceæ (*Closterium*, *Cosmarium*, various diatoms (*Nasica*, *Gomphonema*, *Odontidium*), were placed in well-water containing 1 part per thousand of sodium-azoimide. After eighteen hours not the slightest injurious action could be detected under a magnifying power of 800 diameters. Not until the third day could a slowly progressive fading be detected. Even after ten days living cells could still be detected in the Alga. The dead cells of the *Spirogyra* showed a strong granulation of such an appearance as may be observed in the influence of ammonium salts at 1 part per thousand.

In the diatoms and *Oscillaria* the phenomena of movement did not totally disappear before the fifth day. At the same time the death of the protoplasm of the Desmidiaceæ was recognised.

If the above solution was diluted ten times, and mineral nutrient salts were added (0.1 of each per thousand), the Alga above named remained living even after three weeks, and were healthy. Filaments of *Vaucheria* exhibited distinct growth.

Very different is the behaviour of the same Alga with hydroxylamine and diamide. By these substances, at the same dilution (0.1 per thousand), the Alga are killed within forty-eight hours at furthest, even in a perfectly neutral solution.

3. Experiments with Bacteria.

One portion of a culture solution of the following composition:—Potassium sodium tartrate, 1 per cent; potassium diphosphate, 0.1 per cent; magnesium sulphate, 0.05 per cent; calcium chloride, 0.05 per cent—was mixed with 0.1 per cent sodium azoimide, a second with 0.1 per cent diammonium phosphate, and a third with both these nitrogen compounds together. The three mixtures were then infected with bacteria which had grown in a methylic nutrient solution on exposure to the air. After forty-eight hours the second portion showed a strong bacterial turbidity, whilst the microscope showed a vast quantity of bacteria, which quickly effected the fermentation and combustion of the tartaric acid in the nutrient solution. The two others, even after standing for six weeks, and after repeated infection, remained perfectly clear, and developed not a trace of bacteria. Even when the solutions were diluted fivefold, and infected afresh, there were still no living bacteria. They were thus again diluted twofold, so that they only contained 0.1 per thousand sodium azoimide; 0.5 per cent glucose was added. They were infected again, and let stand for fourteen days in an open flask. No bacterial turbidity appeared, but a few living bacteria were present. That flask which contained ammonia along with the sodium-azoimide displayed a thin film of *Saccharomyces* (probably *S. ellipsoideus*).

(To be continued.)

A Treatise on Manures.—Messrs. Whittaker and Co. have in the press a second edition of Dr. A. B. Griffiths's "Treatise on Manures." It is a little more than two years since the work appeared; therefore, to bring the new edition up to date, it has been necessary to add fifty pages of new matter.

* Ber. Deutsch. Chem. Gesell.

DETERMINATION OF SMALL QUANTITIES
OF ALKALI AND RECOGNITION
OF THE NEUTRALITY OF WATER.

By F. MYLIUS and F. FOERSTER.

(Continued from p. 266).

AFTER a few minutes it is allowed to flow into a second similar parting funnel, where it is shaken with 10 c.c. of aqueous ether in order to remove again the greatest part of the free eosine taken up by the water at the first shaking. The solution thus twice shaken is lastly collected in a flask in order to compare it with a solution of alkaline eosinate of known strength. Such a comparative solution is made up with a number of c.c. of the above-named alkaline solution of iodeosine diluted with water. For comparison solutions are preferred the colouration of which corresponds to 5–20 c.c. of the original solution in 100 c.c. and strata of liquid of 5–15 c.m. in depth. On account of the small extent of these figures, it is often necessary to dilute the coloured solution in a suitable manner. Here, and in measuring out the comparative solution, it must be remembered that the quantity of liquid used for comparison = 110 c.c. For the purpose of comparison, Wolff's colorimeter is very suitable, in which the adjustment of two solutions for equality of colour is effected by regulating the depth of the strata.

As regards the calculation of the determinations which have been carried out by the above-named process, it was already mentioned that we cannot conclude directly the quantity of alkali present from the red colouration of the shaken solution by comparison with a solution of sodium eosinate of known strength and of an equal intensity of colour. Into the watery stratum there passes, as already mentioned, some free eosine, which partly remains there after the second shaking; this introduction is, however, exceeded by the eosine given off to the ether in consequence of the hydrolytic fusion of the alkaline eosinates. Both these influences cannot be calculated, and hence it becomes necessary to multiply the quantity of alkali calculated directly from the red colouration observed by an empirical factor in order to obtain the quantity of alkali really present. In order to find such a factor there were carried out a series of determinations with varying quantities of a solution of soda containing 1.0 m.grm. Na_2O per litre. It appeared that on employing every precaution required by the sensitiveness of the method, equal results were obtained under like conditions, though, as it might be expected, the values found show deviations which may amount to 10 per cent of the total. The following table contains the mean values from a series of separate determinations:—

Quantities of Na_2O employed in thousandth m.grms. in 100 c.c.	Colour observed corresponds to c.c. of eosine solution.	Thousandth m.grm. Na_2O would correspond to the colouration.
0	5.6	—
10	14.5	6.6
15	20.5	11.0
20	25	14.3
25	31	18.8
40	45	29.1
60	60	44.7
80	86	59.5
100	104	72.8

From the above it will be seen that the increase of the red colouration observed corresponds approximately with the quantities of alkali present. In the third column those quantities of alkali are laid down which must be present if all the alkali is present as neutral sodium eosinate; therefore if 1 c.c. of the eosine solution corresponds to the equivalent quantity of soda, i.e., 0.00074 m.grm. Na_2O , the number of the c.c. taken into calculation is that observed with deduction of the 5.6 c.c. eosine

solution required by pure water, as this difference can only be referred to the alkali present. It is observed that the quantities of alkali computed in this manner approximate very closely to the same fraction of that really present, i.e., on the average 72.4. In order to raise this 72.4 to 100 it must be multiplied with $100/72.4 = 1.38$.

Hence 1 c.c. of the alkaline solution of eosine represents—

0.00102 m.grm. Na_2O .
0.00154 " K_2O .
0.00056 " NH_3 .
0.00189 " CaO .

An example will explain what has been said. In the above conspectus we find that the colour observed corresponds to 45 c.c. of the eosine solution; as the "eosine value" of pure water = 5.6, the colour corresponding to the alkali = 39.4 c.c. solution of eosine. If all the alkali were present as neutral sodium eosinate, 1 c.c. of eosine solution would = 0.00074 m.grm. Na_2O ; but in fact 1 c.c. corresponds to 1.38 times this quantity of alkali; that is, to 0.00102 m.grm. Na_2O . Hence 39.4 c.c. correspond to 0.0402 m.grm. Na_2O , and the quantity employed would be 0.0400 m.grm. Na_2O .

How far we arrive at an agreement between the quantities of alkali used and detected will be seen from the following conspectus:—

Potassa.		
Used.		Found
15.16		14.2
30.32		32.1
60.64		58.9
90.96		88.3
151.6		160.1
Ammonia.		
Used.		Found.
10.96		11.4
21.92		20.4
54.84		55.4

(To be continued.)

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY
SAMPLES OF THE WATER SUPPLIED TO LONDON
FOR THE MONTH ENDING OCTOBER 31ST, 1891.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London
Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, *Metropolis Water Act, 1871*.

London, November 7th, 1891.

SIR,—We submit herewith the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from October 1st to October 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined, all were found to be clear, bright, and efficiently filtered.

As a consequence of the exceptionally flooded state of the rivers during the greater portion of the month of October, the character of the water supplied to the Metropolis, in respect to its degree of freedom from organic matter, was on the whole less satisfactory than it has been found for a long time past. The New River Company's supply, though appreciably affected towards the end of the month, maintained a high average standard; while the supply of the East London Company from the Lea, and that of the Chelsea Company from the Thames, were, owing doubtless to the large storage area of these two Companies, not affected by the floods to any notable extent. In the case of the other Thames-supply Companies, in different degrees in different instances, the proportions of organic matter present, as indicated by the degree of colour-tint of the water, and estimated by the combustion and oxidation processes, were appreciably in excess of the proportions habitually met with. The mean proportion of organic carbon present in the Thames-derived supply was 0.197 in 100,000 parts of the water, as against a mean of 0.129 part in the previous month's supply; while, in two samples, the maximum amounts were found to be 0.395 and 0.422 part respectively,—the variation of amount in the other samples examined ranging from 0.143 part to 0.241 part in 100,000 parts of the water.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

OCCURRENCE OF A NATURAL SULPHIDE OF GOLD.

By T. W. T. ATHERTON.

THE existence of gold in the form of a natural sulphide in conjunction with pyrites has often been advanced theoretically as a possible occurrence, but up to the present time this occurrence has, I believe, never been established as an actual fact.

During my investigations on the ore of the Deep Creek Mines, I have found in them what I believe to be gold existing as a natural sulphide. The description of this ore will, no doubt, be of interest to your readers.

The lode is a large irregular one of pure arsenical pyrites, existing in a felsite dyke near the sea coast. Surrounding it on all sides are micaceous schists, and in the neighbourhood is a large hill of granite about 800 feet high. In the lode and the rock immediately adjoining it are large quantities of pyrophyllite, and in some places of the mine are deposits of this pure white, translucent mineral, but in the ore itself it is a yellow and pale olive-green colour, and is never absent from the pyrites.

From the first I was much struck with the exceedingly fine state of division in which the gold existed in the ore. After roasting and very carefully grinding down in an agate mortar, I have never been able to get any pieces of gold exceeding the one-thousandth of an inch in diameter, and the greater quantity is very much finer than this. Careful dissolving of the pyrites and gangue, so as to leave the gold intact, failed to find it in any larger diameter. As this was a very unusual experience in investigations on many other kinds of pyrites, I was led further into the matter. Ultimately, after a number of experiments, there was nothing left but to test for gold as a sulphide.

Taking 200 grms. of pyrites from a sample assaying 17 ozs. fine gold per ton, grinding it finely, and heating for some hours with a solution of sodium sulphide (Na_2S_2), on decomposing the filtrate and treating it for gold I got

a result at the rate of 12 ozs. gold per ton. This was repeated several times with the same result.

This sample came from the lode at the 140 feet level, whilst samples from the higher levels where the ore is more oxidised, although carrying the gold in the same degree of fineness, do not give as high a percentage of auric sulphide.

It would appear that all the gold in the pyrites (and I have never found any apart from it), has originally taken its place there as a sulphide.

The following is an analysis of a general sample of the ore:—

Silica	13.940	p.c.			
Alumina	6.592	"			
Lime	0.9025	"			
Sulphur	16.584	"			
Arsenic	33.267	"			
Iron	27.720	"			
Cobalt	0.964	"			
Nickel			Traces		
Gold			5 ozs.	3 dwts.	8 grs.
Silver			0 "	16 "	0 "

99.969

Nambucca Head's Gold Mining Company,
Deep Creek, N.S. Wales, Oct. 9, 1891.

PROPERTIES OF PRECIPITATES, &c.*

By E. WALLER, Ph.D.

(Concluded from p. 269).

SnS_2 .

Rem.—Usually precipitated by H_2S in acid solution, or by acidifying solutions of alkaline sulpho-stannate. Obtained for purposes of separation, or for determination as SnO_2 after oxidising. Disposition to run through the filter checked by alkaline acetates or nitrates, &c.

Cond.—Solution slightly acid, moderately dilute. Precipitation promoted by acetates, interfered with by alkaline oxalates or oxalic acid.

Sol.—Moderately concentrated acid, especially HCl , dissolve or prevent precipitation. The influence is more marked the more concentrated the acid, or the higher the temperature. Soluble in a boiling solution containing free $\text{H}_2\text{C}_2\text{O}_4$. (Separation from Sb .)

Ign.—If rapidly and strongly heated, some SnS_2 may be volatilised. By moderate heating with access of air, SnO_2 forms without loss. It is, however, usual to assist the oxidation with a few drops of HNO_3 added from time to time.

Ammonium Phosphomolybdate. $12\text{MoO}_3(\text{NH}_4)_3\text{PO}_4$.

Rem.—Yellow, finely-crystalline precipitate. Precipitant $(\text{NH}_4)_2\text{MoO}_4$ in HNO_3 solution. The ratio of MoO_3 to P_2O_5 in the precipitate varies according to the proportion of substances present in the solution (NH_3 , NO_3 , $\text{Fe}_2(\text{NO}_3)_6$, &c.), the proportion of free acid, the kind of acid, the length of time elapsing before filtering, and the temperature at which it is effected. With the same or closely similar conditions, the ratio of MoO_3 to P_2O_5 is essentially the same. Precipitation promoted by agitation. When precipitation is complete, the precipitate settles rapidly after stirring. Precipitated under the conditions described by Emmerton (volumetric determination of P in irons), the ratio of MoO_3 to P_2O_5 is 24 to 1.

Cond.—Solution should be acid with HNO_3 . Too much free HNO_3 retards, or may prevent complete precipitation; too little allows Fe_2O_3 to come down with it, in which case the colour is more orange. An excess of the

* From *School of Mines Quarterly*, xii., No. 4.

precipitant should be present; also at least 10 grms. of NH_4NO_3 for every 0.1 gm. or less of P present. Temperature should be $70-85^\circ\text{C}$. Below 70° the separation is very slow, whereas on boiling (other conditions being right), MoO_3 or Fe_2O_3 may accompany the precipitate. Reducing agents, organic acids, silica, chlorides, and HCl , should be absent. H_2SO_4 and sulphates retard precipitation. If the precipitate is to be dissolved for volumetric estimation, in a solution of material containing but little iron, some iron should be added to give correct results, or the standard should be obtained with material of the same character.

Sol.—Readily dissolved by NH_4OH and other alkalis; also by alkaline phosphates. If the ammonia is too strong, however, the solution will be turbid with $(\text{NH}_4)_2\text{MoO}_4$. Dissolved or decomposed by water alone, the more readily the higher the temperature. Precipitation prevented by tartaric acid or organic substances of that class. Somewhat soluble in HCl , or moderately strong H_2SO_4 and HNO_3 . Insoluble in weakly acid solutions and acid solutions of NH_4 salts. Solution for washing should contain 1 per cent HNO_3 and 10 per cent NH_4NO_3 , or a corresponding amount of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$.

Contam.—Arsenio-molybdate, silica, Fe_2O_3 , TiO_2 .

Arsenio-molybdate precipitates the less readily the lower the temperature. By allowing the solution to stand for about two days at 40°C ., the phospho-molybdate may be precipitated free from arsenic. When present, however, As is separated either before or after.

Silica, either as hydrated SiO_2 or as silico-molybdate (the existence of which is disputed), may be present. By allowing the ammonia solution to stand for some time after addition of NH_4Cl , the flocculent silica separates and may be filtered off.

Fe_2O_3 in the precipitate often causes it to separate in crusts on the sides of the beaker. On attempting to dissolve in ammonia, yellow to red $\text{Fe}_2(\text{OH})_6$ mixed with $\text{Fe}_2(\text{PO})_2$ remains undissolved. After washing with ammonia this residue is dissolved in HNO_3 , the solutions united and re-precipitation effected, after acidifying with HNO_3 .

Hydrated TiO_2 (which retains P_2O_5) can be separated by fusing the portion insoluble in ammonia for some time with Na_2CO_3 (*vide* Na_2TiO_3), leaching with water, and in the water solution re-precipitating with the molybdate reagent.

SILICA.

Rem. and Cond.—On adding an excess of mineral acid to a solution containing a silicate, free silicic acid containing indefinite amounts of water is formed, partially or entirely soluble. On evaporation H_2O (of constitution) is removed and insoluble SiO_2 is separated, which may be filtered off after digestion with diluted acid. HCl is the acid most frequently used. When HNO_3 is used, regard must be had to the fact that certain nitrates ($\text{Fe}_2(\text{NO}_3)_6$, &c.), are decomposed at the temperature usually employed to drive out the last portions of the water ($110-130^\circ\text{C}$.), and are not readily re-formed by digestion with diluted HNO_3 . The heat is usually maintained until there is no perceptible odour of acid. With H_2SO_4 , the heat is continued until fumes of SO_3 are evolved, indicating that H_2SO_4 is the only free acid remaining. If the heat has not been sufficiently prolonged or intense, the separated silica may be flocculent and filters with difficulty, or some may remain soluble.

If the heat has been too high, the conditions may have favoured a re-combination of silica with the bases, and consequent soluble silica (analogous to the action by fusion). The temperature which can safely be applied may be put at $110-120^\circ$.

According to Gilbert (*Technical Quarterly*, February, 1890), when only Ca and alkalis are present, the temperature of drying may be carried up to 280°C . without detriment; but if Mg is present, re-combination of the

bases with the silica is best prevented by drying at 120°C . Some alumina almost invariably remains with the silica if Al is present in the solution.

Sol.—Dissolved by boiling or fusing with fixed alkalis, caustic or carbonated. Insoluble in water and acids (HF excepted).

Contam.—Insoluble sulphates (PbSO_4 , BaSO_4) removed by digestion with concentrated H_2SO_4 , and filtering through asbestos. (For other solvents of these substances, *vide sup.*) In some cases CaSO_4 , removable by digestion with HCl and NH_4Cl . The precipitate may also contain a form of $\text{Fe}_2(\text{SO}_4)_3$ (when separated from concentrated H_2SO_4) which dissolves in dilute H_2SO_4 with some difficulty, but is readily soluble in HCl .

SnO_2 or Sb_2O_3 may be retained, as well as TiO_2 (possibly combined with P_2O_5) and ferric or aluminic oxides or basic salts. TiO_2 tends to hold P_2O_5 , Al_2O_3 and Fe_2O_3 in the precipitate. To avoid error in such cases the SiO_2 should be determined by loss, adding HF or NH_4F (and in any case H_2SO_4), igniting off SiF_4 , and weighing again. This treatment is advisable whenever Al_2O_3 is present in the solution in any quantity.

Ign.—Precipitate is very light and fine, and readily carried off by flame, requiring especial precaution on igniting. After ignition, the precipitate will absorb appreciable amounts of water if exposed to air containing moisture.

ON THE OCCURRENCE OF NITROGEN IN URANINITE, AND ON THE COMPOSITION OF URANINITE IN GENERAL.*

By W. F. HILLEBRAND.

(Continued from p. 257.)

TABLE III.—Uraninite from Colorado and North Carolina.

	IX. Colorado.			X.	XI.
	a.	b.	Mean.	North Carolina.	North Carolina.
UO_3	25.26	—	25.26	50.83	44.11
UO_2	58.47	58.56	58.51	39.31	46.56
TiO_2	trace	trace	trace	—	—
ZrO_2	7.32	7.85	7.59	—	—
ThO_2	—	—	—	2.78	—
CeO_2	0.22	0.22	(a) 0.22	0.26	—
$(\text{LaDi})_2\text{O}_3$..	—	—	—	0.50	3.04
$(\text{YEr})_2\text{O}_3$..	—	—	—	0.20	—
PbO	0.69	0.71	0.70	4.20	4.53
ZnO	0.43	0.44	0.44	—	—
FeO	0.32	—	(b) 0.32	trace	—
MnO	0.16	—	0.16	—	—
CaO	0.84	0.85	0.84	0.85	0.23
MgO	trace?	—	trace?	—	—
Alk	trace?	—	trace?	0.30	0.25
H_2O	1.96	—	1.96	1.21	undet.
N	0.15	—	(c) 0.15	(d) 0.37	undet.
SiO_2	2.76	2.82	2.79	0.08	0.13
P_2O_5	0.22	—	0.22	?	—
As_2O_5	0.43	—	0.43	—	—
CuFeS_2	0.12	—	0.12	—	—
FeS_2	0.24	—	0.24	—	—
Insol.	—	—	—	0.10	0.06
Total	—	—	99.95	100.99	98.91
All U as UO_2 ..	—	—	82.36	87.31	88.21
Sp. gr.	—	—	8.068	8.086	9.492
Temp., $^\circ\text{C}$. ..	—	—	20	15.8	20

* From "Bulletin No. 78, U.S. Geological Survey, 1889-90." An abstract of this paper was published in the *Am. Jour. Sci.*, vol. xl, p. 384.

TABLE IV.a.—Uraninite from Norway.

	XII. Anneröd.		XIII. Elvestad.		XIV. Elvestad.		XV. Skraatorp.		XVI. Huggenäsliken.		XVII. Arendal (h)	XVIII. Arendal.
	a.	b.	a.	b.	a.	b.	a.	b.	a.	b.		
UO ₃	30'56	30'70	25'34	$\left\{ \begin{smallmatrix} 25'49 \\ 25'26 \end{smallmatrix} \right\}$	22'02	22'06	31'93	32'08	35'52	35'57	41'71	26'80
UO ₂	46'20	46'07	50'76	$\left\{ \begin{smallmatrix} 50'62 \\ 50'84 \end{smallmatrix} \right\}$	43'05	43'01	43'95	43'81	43'36	43'39	24'18	44'18
ZrO ₂	0'06	—	0'08	—	—	—	—	—	—	—	—	—
ThO ₂	6'00	—	8'48	—	—	—	8'98	—	6'59	—	—	4'15
CeO ₂	0'18	—	0'21	—	8'43	—	0'17	—	0'20	—	3'66	none
(DiLa) ₂ O ₃ ..	0'27	—	0'26	—	—	—	(f) 0'36	—	0'23	8'13	—	(i) 0'67
(YEr) ₂ O ₃ ..	1'11	—	(c) 1'10	—	—	—	0'97	—	1'03	—	9'76	9'05
PbO	9'04	—	10'06	—	8'58	8'58	9'50	9'42	9'46	$\left\{ \begin{smallmatrix} 9'45 \\ 9'41 \end{smallmatrix} \right\}$	10'54	10'95
CaO	0'37	—	0'77	—	0'37	—	0'36	—	0'41	0'41	1'06	0'61
MgO	—	—	—	—	0'13	—	—	—	0'13	—	0'10	0'04
Alk	trace	—	trace	—	—	—	trace	—	—	—	0'23	0'15
H ₂ O	0'74	—	0'73	—	0'74	—	0'77	—	0'79	—	1'23	undet.
N	1'18	(b) 1'15	(d) 1'29	—	1'08	—	1'03	—	1'08	—	undet.	1'24
Fe ₂ O ₃	0'25	—	0'21	—	0'30	0'31	0'09	—	0'32	0'31	0'03	0'24
MnO	—	—	0'06	—	—	—	—	—	—	—	—	—
SiO ₂	0'22	—	0'38	0'39	0'28	0'30	0'53	—	0'45	$\left\{ \begin{smallmatrix} 0'51 \\ 0'50 \end{smallmatrix} \right\}$	0'90	0'50
P ₂ O ₅	0'02	—	0'04	—	trace	—	(?)	—	trace	—	—	trace
Insol. ...	(a) 4'42	—	0'44	0'46	(e) 15'50	15'41	(g) 1'54	—	0'41	0'43	1'10	1'19
All U as UO ₂	75'06	—	74'69	—	63'84	—	74'10	—	76'90	76'98	63'57	69'49

(a) The gangue was mainly columbite, and contained a total of 61 FeO by trial on a separate portion. The columbite could be pretty well separated from the other and lighter gangue matter after solution of the uraninite in nitric acid, and it was found that of the total FeO, 0'30 belonged to the columbite and 0'31 to the other gangue constituent. This latter was dissolved by the acid in UO₂ determinations, while the columbite was not; hence a correction has been made for 0'31 FeO representing 0'58 UO₂.

(b) The first result by fusion with NaKCO₃, the second by solution in HCl. Another result of 1'28 by H₂SO₄ was the first quantitative determination of nitrogen made, and was probably too high through leakage of air into the receiver.

(c) Molecular weight, 277.

(d) By fusion with NaKCO₃. The first result was obtained by H₂SO₄.

(e) Almost entirely columbite.

(f) Perhaps not fully freed from ThO₂.

(g) Mainly a phosphate.

(h) A brief but brisk effervescence was produced by acids. The deficiency in the analysis, 5'50 per cent, was supposed to be satisfactorily accounted for as CO₂; a portion of it, however, is probably to be credited to nitrogen.

(i) The ignited oxides differed in appearance from the mixtures of La₂O₃ and Di₂O₃ obtained in all other analyses, being nearly colourless.

TABLE IV.b.—Means of Analyses in Table IV.a.

	XII. Anneröd.	XIII. Elvestad.	XIV. Elvestad.	XV. Skraatorp.	XVI. Huggenäsliken.	XVII. Arendal.	XVIII. Arendal.
UO ₃	30'63	25'36	22'04	32'00	35'54	41'71	26'80
UO ₂	46'13	50'74	43'03	43'88	43'38	24'18	44'18
ZrO ₂	0'06	0'08	—	—	—	—	—
ThO ₂	6'00	8'48	—	8'98	6'63	—	4'15
CeO ₂	0'18	0'21	8'43	0'17	0'20	3'66	none
(DiLa) ₂ O ₃ ..	0'27	0'26	—	0'36	0'23	—	0'67
(YEr) ₂ O ₃ ..	1'11	1'10	—	0'97	1'03	9'76	9'05
PbO	9'04	10'06	8'58	9'46	9'44	10'54	10'95
CaO	0'37	0'77	0'37	0'36	0'41	1'06	0'61
MgO	—	—	—	—	—	—	—
Alk	trace	trace	0'13	trace	0'13	$\left\{ \begin{smallmatrix} 0'10 \\ 0'23 \end{smallmatrix} \right\}$	0'04
H ₂ O	0'74	0'73	0'74	0'77	0'79	1'23	undet.
N	1'17	1'28	1'08	1'03	1'08	undet.	1'24
Fe ₂ O ₃	0'25	0'21	0'30	0'09	0'32	0'03	0'24
MnO	—	0'06	—	—	—	—	—
SiO ₂	0'22	0'38	0'29	0'53	0'49	0'90	0'50
P ₂ O ₅	0'02	0'04	—	(?)	trace	—	trace
Insol. ...	4'42	0'45	15'45	1'54	0'42	1'10	1'19
Total	100'61	100'21	100'44	100'14	100'09	94'50	99'77
Sp. gr.	8'893	9'145	8'320	8'966	8'930	7'500	—
Temp. °C. ..	21'6	17	29'7	20	28'2	26'8	—

Notes to Table III. p. 279.

- (a) Lanthanum not tested for.
- (b) Calculated from total iron after deducting that required by pyrite and chalcopyrite.
- (c) By fusion with NaKCO_3 . H_2SO_4 failed to decompose entirely in nine days at 100°C .
- (d) Mean of 0.38 by fusion with NaKCO_3 and 0.35 by H_2SO_4 .

IX. From a specimen in the National Museum from near Black Hawk, Colorado, where the mineral was originally identified by Mr. Richard Pearce about 1872. A very few tons represented the total product of the mine in uraninite, which was shipped to Great Britain for treatment.

This variety, differing in some respects so markedly in composition from all other known uraninites, is also distinguished from the other North American occurrences by its utter want of crystalline form. The specimen examined was largely contaminated with pyrite and chalcopyrite; in places it consisted of these alone, in others of pretty pure uraninite. But the purest of the latter was seamed with minute cracks filled with sulphides. A section as thin as possible showed under the microscope absolutely no other impurity. The material used for analysis was obtained, after sifting to grades of fineness, by first panning and then exposing the partly cleaned grains in a specially devised apparatus to an upward current of water, through which the heavy uraninite fell while the sulphides were held up. It was then further purified by most laborious hand-picking under the lens. Even so it was impossible to free it altogether from sulphides, as the analysis shows, and this is especially unfortunate because of the uncertainty which is thereby thrown upon the UO_2 estimations. These, as above given, include the effect of any hydrogen sulphide and ferrous iron formed by the solvent action of sulphuric acid and of ferrous oxide possibly already existing. That they are not far from correct, however, is evidenced by a gravimetric estimation of UO_2 after separation by hydrofluoric acid, where sulphides and ferrous iron would be without effect, which gave 58.24 per cent UO_2 . Another element of uncertainty in the volumetric determination is caused by want of knowledge of the condition in which arsenic is present. It has been assumed as As_2O_3 , mainly for the reason that when even dilute nitric acid was used for dissolving, hydrogen sulphide precipitated the arsenic only after a considerable time. The condition of the zinc is likewise unknown. Its most natural form would be as sulphide; but as the sulphur was insufficient for the zinc alone, the negative element has all been credited to pyrite and chalcopyrite.

The analysis presented considerable difficulty. It was found that, on solution in nitric acid, a dirty white residue was left which contained silica, zirconia, and phosphoric acid, and that on boiling a further precipitate of zirconia containing phosphoric acid came out. None of the silica was present as quartz, for the residue in nitric acid was entirely free from grit; nor can it have been combined with zirconia as zircon, for the same reason and because the latter is insoluble. But for the phosphoric acid it is probable that the residue would have held no zirconia, since a very little of the former seems able to carry down much of the latter, even in a very acid solution. The silica given in the analysis represents both that in the residue and that subsequently obtained by evaporation after boiling and filtering. The rest of the zirconia and the other earths were separated from uranium by potassium sulphate.

X., XI. From the Flat Rock mine, Mitchell County, North Carolina, through Mr. W. E. Hidden. Entirely unaltered uraninite seems never to have been found in North Carolina, and no analysis of it appears to have been made, though its alteration products have received attention. The crystal form of the original mineral is

often preserved in the pseudomorphs, and it is decidedly more cubical than that of the Connecticut crystals, which are usually octahedral in habit. Even the least-altered material, though it may present a perfectly fresh aspect, is seamed in all directions by microscopic cracks filled with yellow alteration products. Such was the character of the piece used for analysis X., which was undertaken for the purpose of ascertaining whether or not the North Carolina mineral contained rare earths. In order to observe the effect of a weak solvent another lump was immersed for several days in very dilute cold hydrochloric acid, whereby it gradually fell into a fine powder, which was washed, dried, and analysed with the results given under XI.

XII. The original bröggerite, from Gustavsgruben, Annerröd, near Moss, received from Prof. W. C. Brögger, who writes "Es ist das originale Vorkommen des Bröggerit Blomstrands."

XIII. Likewise from Prof. Brögger, labelled "Uraninit, Elvestad b. Moss." In addition Prof. Brögger writes, "So viel ich weiss, von derselben Stelle wie das Originalmaterial Lorensens."

XIV. to XVIII. From Prof. A. E. Nordenskiöld, through Prof. F. W. Clarke, of the U.S. Geological Survey. These specimens all bore, with one exception erroneously as the analyses show, the name cleveite, on labels of the Royal Museum of Stockholm; XIV. was from Elvestad, XV. from Skraatorp, XVI. from Huggen-åskilen, all being localities near Moss, and XVII. and XVIII. were from Arendal. The Arendal material was not in separate crystals and fragments like the others, but was inclosed in the original matrix of felspathic rock. Of this there were three or four small pieces, from one of which some very inferior-looking material was extracted. It had every appearance of being much altered, which the evolution of carbonic acid by acids and the abnormally low percentage of UO_2 seemed so fully to demonstrate that no particular pains were taken beyond separating the earths from uranium and dividing them roughly into two groups. The material was in any case insufficient for a carbonic acid estimation. Later it became of interest to learn if this apparently greatly altered material contained nitrogen, and to this end further material was extracted from another of the pieces of rock. Its analysis unexpectedly gave the results under XVIII., the water alone being undetermined for want of material.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

November 20th, 1891.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

DR. PHILIPPE A. GUYE gave a short account and discussion of the various forms which have been given to the general equation expressing the behaviour of liquids and gases under different conditions of volume, temperature, and pressure, by Van der Waals, Clausius, Sarran, Violi, Heilborn, and Tait. He first considered the equation of Van der Waals, which, although only an approximation to the true one, may be made to lead to numerous important deductions. He then showed that of the various more exact formulæ proposed, that of Sarran is the simplest, and may be used with less expenditure of time and trouble than any of the others. In conclusion he insisted on the necessity of experimental researches as the only means of arriving at a definite conclusion as to which of the various formulæ is the true one; such researches should involve determinations, as exact as

possible, of the critical constants, and of isotherms at high temperatures and great pressures.

Prof. RAMSAY inquired whether the constants in the formula of Clausius had any physical meaning or were they merely numbers?

M. GUYE, in reply, said that although some of the constants in the improved formulæ had physical interpretation Van der Waals' equation was the only one in which all the constants had precise physical significations.

Prof. RÜCKER said it was only necessary to look at the formulæ to see how important a factor Van der Waals' expression had been in later developments of the subject. Although it did not agree with experiment under all conditions, particularly at small volumes, yet it was a close approximation over a considerable range, and was the only formula in which all the constants had definite physical meanings. Prof. Tait had pointed out that the number of constants were too few to fully represent the facts, for by following Andrews' reasoning he had shown that about the critical point a straight line cuts the isotherm in five points. Nevertheless, during the last twenty years all the so-called improved formulæ were modifications of Van der Waals' expression, and this, he thought, showed how valuable the original formula was.

Prof. FITZGERALD said he once tried how far Clausius' formula agreed with the experimental results published by Messrs. Ramsay and Young, and after several months' work relinquished it on account of the tremendous labour involved. He thought that such complicated formulæ retarded rather than advanced science; simple ones (even if less accurate) were likely to lead to greater advancement.

Prof. CAREY FOSTER remarked that the expression $p \cdot v = RT$, which is nearly true for gases, was the starting-point of all subsequent advances. Van der Waals had arrived at a still closer approximation by taking into account the volume occupied by the particles and their mutual pressure.

The PRESIDENT said Van der Waals' memoir had been adversely criticised because of its supposed insufficient recognition of Andrews' investigations on the subject. Better acquaintance with the work had, however, shown this criticism to be undeserved.

Dr. C. V. BURTON read a paper on "*A New Theory concerning the Constitution of Matter.*" It is assumed that it is possible to have in the ether a distribution of strain which is itself in equilibrium. Such a distribution is called a "strain-figure." An atom is looked upon as an aggregation of strain-figures, the possible varieties of strain-figures (and hence of atoms) being limited by the conditions of equilibrium, and the sizes of possible strain-figures dependent on the coarse-grainedness of the turbulent motion or other structure of the ether.

The motion of matter is considered to be merely the transference of a strain distribution from one portion of the ether to another. This the author illustrated by causing a loop to travel along a rope, the loop being regarded as a strain-distribution, which is propagated along the rope whilst the rope itself is not transferred. Such transference may occur without encountering any resistance, and the strain-figure will retain the same form, provided the velocity is small compared with that at which gravitation is propagated.

The equations of motion of a strain-figure are deduced and are shown to be identical with those of ordinary matter, provided certain conditions of symmetry are realised.

It is also shown under what conditions an atom consisting of strain-figures would have a finite number of degrees of freedom, and some attempt is made to examine how gravitation and other attractions might follow from a distribution of stress in the strained ether. An inquiry is also made into the reason why elements have fixed properties, and their transmutation is discussed.

Prof. FITZGERALD, referring to the elastic solid theory

of the ether, said Sir W. Thomson's more recent papers had thrown considerable doubt upon it. The propagation of strain-figures was, he thought, a case of wave motion. In his lectures he had likened the passage of matter through space to that of a drop of water through ice, the ice in front melting and the rear of the drop freezing as the liquid state progressed.

Many points raised in the paper were, he said, very interesting, and the suggestion that the discrete nature of atoms is the result of the coarse grainedness of matter, very good. On the other hand he considered the static treatment of strain-figures improper, for the ultimate conditions must be kinetic.

Dr. O. LODGE agreed with Prof. Fitzgerald in regarding the motion of the loop along the rope as a wave-motion, whose velocity of propagation is equal to that of the loop. A similar case occurs when a ring of rope is spinning, and has a pulse impressed on it at one point, for the pulse travels at the same speed as the rope.

A paper on "*A Permanent Magnetic Field,*" by Mr. W. HIBBERT, was postponed until next meeting.

CORRESPONDENCE.

THE SAPONIFICATION OF BEEF FAT.

To the Editor of the Chemical News.

SIR,—I observe (page 273) that Dr. Johnstone is still dissatisfied with my statement that he had recently published experiments (*Analyst*, xvi., 26) according to which beef fat requires 23 per cent of caustic potash for its saponification. As I pointed out in a previous letter, Dr. Johnstone's position is similar to that of a man who has stated that he was born in 1868, and then objects to others holding that his age is now twenty-three.

As Dr. Johnstone asks me to explain the exact meaning of my "most unaccountable and uncalled-for criticism," I have much pleasure in reminding him that chemists are in the habit of expressing the amount of alkali required to saponify a fat in terms of caustic potash (KHO), and that they do this whether caustic potash or caustic soda was actually used to effect the saponification. Whether Dr. Johnstone's protest is sincere, and his grievance serious or paltry, may be judged from the fact that in the very letter in which he formulates his complaint, Dr. Johnstone himself "calculates the glyceryl (C_3H_5) from the amount of KHO consumed," though he actually employed NaHO for the saponification!

In the two experiments on beef fat quoted by Dr. Johnstone, the volume of normal caustic alkali (NaHO) required for saponification was 10.54 and 10.57 c.c., the average of these figures being (according to Dr. Johnstone) 10.56 c.c. But 10.56 c.c. of normal caustic alkali corresponds to $0.0561 \times 10.56 = 0.5924$ grm. of real KHO required for the saponification of 2.5 grms. of beef fat, or 23.696 per cent.

Not having analysed the sample of beef fat in question, I should not presume to pronounce Dr. Johnstone's figures inaccurate. I simply point out that his result (23.7 per cent of alkali, in terms of KHO, required for saponification) is not in accordance with the united experience of other observers that the "alkali-number" for beef fat ranges from 19.3 to about 19.8 per cent; and, as Dr. Johnstone's figures were originally given in an article (*Analyst*, xvi., 26) bristling with anomalies, one is disposed to receive them with considerable reserve. There is no "prejudice" in the question at all. It is simply that the balance of evidence is enormously against Dr. Johnstone, and the probabilities equally great that his figures are erroneous.

That Dr. Johnstone does not claim that his method of operating gives anomalous results is evident from his

statement (*Analyst*, xvi., 27) that "working in this manner an accurate estimation of the amount of alkali required for saponification is obtained, and from which (sic) the Koettstorfer number of the fat is readily calculated."

It is difficult to understand Dr. Johnstone's object in quoting his figures, original and recent, for the total percentage of fatty acids obtained from the beef fat; and the course is objectionable as being liable to obscure the actual point at issue. Dr. Johnstone is perfectly aware that I have not even referred to his determinations of fatty acids, much less ridiculed or described them as anomalous or inaccurate; nor have I hitherto commented on his annexation of the name "glyceryl" for his imaginary radical C_3H_2 . It is a matter which chemists can all appreciate for themselves.—I am, &c.,

ALFRED H. ALLEN.

Sheffield, November 28.

"ALLOTROPIC" SILVER.

To the Editor of the Chemical News.

SIR,—My attention has just been directed to the communication on this subject by Mr. Carey Lea, called forth by some remarks of mine in the Cantor Lectures delivered last spring before the Society of Arts. I should be extremely sorry if Mr. Carey Lea imagines—as would appear from the tone of his communication—that I desired in any way to detract from the value of his most interesting observations. He is labouring under a complete misapprehension if he supposes that I intended to call in question the existence of the coloured compounds or modifications of silver with which he has made us familiar. He is, moreover, inaccurate in stating that my strictures were not based on any "adequate study of the subject," and that "no experimental support of any sort is given." If he will do me the favour of turning to the lectures in question he will find that my statement was: "After carefully considering the conditions of formation, and after repeating some of the experiments, I must say that there appears to me to be no sufficient evidence that these coloured forms consist of the pure metal. On the contrary, all the evidence goes to show that some impurity is present, &c." I may add that, following Mr. Carey Lea's instructions, I have not had the slightest difficulty in preparing the gold-coloured product; with the soluble or colloidal silver I have not been so successful. I freely confess, however, that my experiments have not been numerous in this direction. But since other investigators have succeeded in preparing the "soluble silver" I must attribute my own failure to hurried work or to some violation of Mr. Carey Lea's instructions. I may state also that I am not singular in this failure to produce the "soluble" form, as several other and more experienced operators have met with the same negative results. Mr. Carey Lea would be conferring a boon upon large numbers of chemists in this country who are interested in his work if he would favour us with more explicit instructions.

The facts are that Mr. Carey Lea, by reducing silver salts under certain conditions, has produced certain coloured products which contain a large percentage of silver and a small percentage of other substances. None of the evidence goes beyond this,—not even the most recent contribution to the subject by Schneider, which appears in the number of the *Berichte* just received. One of these products is soluble in water.

Now, I never called in question the existence of these compounds; I did not even bring forward my own and other experimenter's failures as negative evidence. I only thought it right to caution my audience against applying the term "allotropic silver" to these products. I venture to reiterate that caution now in the hope that Mr. Carey Lea will admit its justice. Allotropy I under-

stand to denote "the appearance of one and the same substance (italics mine) in several different states, distinguished from each other by different properties," (*Watt's Dictionary*, Morley and Muir, vol. i., page 128). How, then, can we apply this term to products which have not yet been shown to be "one and the same substance," viz., silver?

If Mr. Carey Lea will prepare specimens of his gold-coloured silver or colloidal silver possessing all the properties of these substances, and containing 100 per cent of silver, I will admit the applicability of his term. In the meantime I consider the designation "allotropic silver" to be premature and apt to mislead. In other words I must remain, and I think other chemists will remain with me, in the same position as that which I felt it necessary to take in the Cantor Lectures.—I am, &c.,

RAPHAEL MELDOLA.

Finsbury Technical College,
Nov. 27, 1891.

STUDIES OF SAPONIFICATION.

To the Editor of the Chemical News.

SIR,—In one of his recent letters to you Mr. Allen said that he was attempting to repeat my experiment of heating slaked lime with butter-fat, and, under cover of asking for directions in order to get over an imaginary practical difficulty, contrived to insinuate a contradiction of the initial fact which I had observed and announced.

That initial fact is, that when dry hydrate of lime and dry butter-fat are heated together in an open vessel in the water-bath, chemical action takes place in the absence of any solvent. It is very possible, indeed, that under these conditions a *complete reaction* may not take place, but my experiment showed that a very considerable quantity of the butter-fat had undergone chemical change, and that fact alone is noteworthy and of some importance.

The proof of the occurrence of the chemical action is the loss of weight which I recorded. Inasmuch as butter-fat is not volatile in the water-bath, and hydrate of lime is neither volatile nor decomposable in the water-bath, it is obvious that the escape of any volatile material must indicate the occurrence of chemical change.

Now, to speak quite plainly, I want to know whether Mr. Allen found the loss of weight, or whether he found that there was no loss, or whether he considered that the fact of loss of weight was too trivial to be worthy of his attention.

Instead of an answer to this question, all that I have hitherto been favoured with is the statement that so far as is known, "simply melted butter with slaked lime in suspension" is all that has been observed. Under these circumstances Mr. Allen will understand that his four or five columns of criticism of the opening portion of my paper read to the Society of Chemical Industry in January is looked upon as amusing, but not otherwise as requiring my immediate attention. At present I shall content myself with pointing out that the possibility of action between the carbonic acid of the atmosphere and the materials heated in the open platinum dish was before my mind when I carried out the experiment on saponification by means of dry hydrate of lime, and I ascertained that, like dry hydrate of potassium, dry hydrate of lime is inactive towards carbonic acid. I took much trouble to ascertain the behaviour of the lime, and in one of my experiments found that after a year's exposure to the atmosphere, a specimen of slaked lime was found to contain only 1·4 per cent of carbonic acid.

Towards the end of his paper Mr. Allen makes a statement of a "peculiar and strictly personal" kind. I invite him to refer to the *Chemical Society's Journal*, date 1867, p. 170, where he will find a paper of mine on the "Titration of Compound Ethers," which will probably open his eyes to the fact that some of the "improvements in the analytical

methods of examining fats," which he and his friends imagine to be new, were anticipated by me nearly a quarter of a century ago, and that, being the inventor of the method to which he refers, I am more keenly alive to its limitations than some of those persons who are using it daily in a machine-like manner.—I am, &c.,

J. ALFRED WANKLYN.

Nov. 30, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 20, November 16, 1891.

Formation of Hydrazin and Azohydric Acid.—MM. Berthelot and Matignon.—A thermo-chemical study. The authors regard hydrazin as a feeble base comparable to ferric oxide, the neutralisation-heat of which is much below that of ammonia and even of hydroxylamine. These three bases represent the three hydrides of nitrogen, but they are not strictly comparable, their condensation being unequal, and one of them constituting a stable hydrate which tends to increase its alkaline character. Azohydric acid, or diazamine N_2H , is, when diluted, an acid comparable in energy to the amidic acids and superior to hyponitrous acid.

Oxidation of Nickel Carbonyl.—M. Berthelot.—This compound behaves like a true organic radicle. It may be preserved in a bottle under a layer of water without alteration, so long as the air does not penetrate. If air finds access the compound is slowly oxidised, forming at the lower part a layer of nickel oxide of an apple-green.

Action of Light upon Ruthenium Peroxide.—A. Joly.—This compound, RuO_4 , improperly called hyper-ruthenic acid may be preserved indefinitely in a sealed tube if perfectly dry. The least trace of water decomposes it, forming an intermediate oxide, Ru_2O_5 , with escape of oxygen. The sides of the tube, if not kept in total darkness, assume a metallic lustre, which is proved by experiment to be due to light alone. The product of the reduction of the peroxide is the tetroxide, RuO_3 .

Certain Saline Compounds of the Lower Oxygen-Compounds of Ruthenium with Ruthenic and Heptaruthenic Acids.—A. Joly.—Potassium ruthenate is a new "mineral chameleon." If the heptaruthenate is heated to 440° in a vacuum, it is abruptly decomposed, liberating oxygen, being converted either into a mixture of ruthenate and ruthenium dioxide, or into a compound of potassium with a lower oxide. If these decomposition products are kept at 440° for a sufficient time they react upon each other, yielding a black, crystalline compound, quite distinct from the dioxide. Its composition is that of an acid salt, $KO, 6Ru_2O_5$. Water removes from the mixture potassa and potassium ruthenate. Sodium heptaruthenate, $NaO, Ru_2O_7 + 2HO$, if heated to 440° , suddenly loses oxygen and water, and if treated with water and orange ruthenate and soda are dissolved, and there remains a black, crystalline powder, the composition of which is close upon $NaO, 3Ru_2O_5$. Barium ruthenate, BaO, RuO_3 , behaves differently at 440° . Oxygen is lost, and the residue, BaO, Ru_2O_5 , is a ruthenite, which, from its reactions, cannot possibly be considered as a mere mixture of baryta and of the dioxide.

Iodonitric and Bromonitric Platinum Salts.—M. Vèzes.—The author has previously described several platinum chloronitrates and bromonitrates, between the platinonitrite $Pt_4NO_2K_2$ and the saturated haloid salt $PtX_4, K_2X_2 (X = Cl, Br)$. In hot solutions of iodonitrates

the iodine in these bodies is displaced by nitrous products, so that the most stable term of the iodine series is the platinonitrite and not the iodonitrate. The author has obtained potassium nitrosoiodoplatinate, PtI_3, NO, K_2I_2 ; potassium platitetraiodonitrite, $PtI_4, 2NO_2, K_2$, and potassium bromonitrite, $Pt, 2NO_2, K_2, Br_2 + H_2O$.

The Colouration of the Solutions of Cobalt, and the State of the Salts in these Solutions.—A. Etard.—The author expresses his conclusions by means of the graphic method.

Nitrised Milk.—Leo. Vignon and P. Sisley.—The authors find that the yellow colouration which nitric acid occasions in silk is best obtained by dipping and rapidly smoothing out the silk for about a minute in a mixture of water and nitric acid, specific gravity 1.133 at 45° . After washing in a large excess of water the silk preserves a very characteristic yellow colour, fast to air and light; the colour is much darkened on immersion in alkaline liquids, but may be restored to its original shade by treatment with acids. Pure nitric acid under the above conditions does not colour silk. If a little sodium nitrite is added to pure nitric acid the yellow colour is produced. The reaction, which gives a fast yellow colour on silk, requires the presence of NO , NO_2 , or NO_2H , and contact with nitric acid as an oxidiser.

Moniteur Scientifique, Quessenneville.
Series 4, Vol. iv., Part 2, No. 588.

Synthesis of Citric Acid.—A. Haller and A. Held.—Syntheses of this acid have been previously effected by Grimaux and Adam, then by Prof. Kekulé, and lastly by Herr Dunschmann. The present authors demonstrate the conditions under which may be effected the synthesis of acetondicarboxylic ether, and subsequently that of citric acid. The synthetic citric acid presents all the physical, organoleptic, and chemical characters of the natural acid. The crystals melt at 100° .

Azohydric Acid, N_3H , or Azoimide.—Herr Th. Curtius.—The author has obtained this compound, which in all its reactions behaves like a hydracid of the haloid family. It is a gas of a peculiar and very pungent odour. It is energetically absorbed by water, and even in dilute solutions it irritates the mucous membranes and occasions headache. It reddens litmus paper, and forms with gaseous ammonia dense white fumes. In a 7 per cent solution it dissolves iron, zinc, copper, aluminium, and magnesium, with a tumultuous liberation of hydrogen. More concentrated solutions seem even to attack gold and silver, for the liquid becomes red. Silver and mercurous nitrates give with dilute azohydric acid precipitates of silver and mercurous azoimide. Azohydric acid does not precipitate the other metallic salts.

Researches on the Devitrifying and Dissolving Action of Water upon Acids.—(No author's name).—The easy devitrification of a glass is not simply due to an excess of lime, but is a function of the ratio existing between simple sodium silicate and acid calcium silicate. This proportion is 0.40 in stable glass, and 0.28 in glasses which are easily devitrified. Glasses with multiple bases are the less easily vitrified the greater the number of bases entering into their composition. It will be easy for the glass-makers to obtain calcareous clays of such a composition that for bottles it will be merely necessary to add sand and a little alkali. For optical glass alumina and iron must be absolutely rejected, and the only available materials are silica, lime, and alkali. From 100 grms. of glass used for glow-lamps water dissolved 3.974 grms. of alkali, besides traces of alumina, ferric oxide, and lime.

On Tanning Woods.—J. J. Arnaudon.—Carolina sumac, the leaves of *Rhus glabra*, is used in tanning, but its proportion of tannin is not stated. Copaline sumac

(*Rhus copalinum*) contains rather less tannin than *Rhus glabra*. Both the above species of sumac are of American origin. Chinese sumac (*Rhus semialata*) is the bark of a tree upon which the Chinese gall-nuts are produced. Fustet or scotano is the wood of *Rhus cotinus* (known in England as young fustic). The best quality comes from Greece and the Ionian Islands. Sumac of Tezera, or of Africa (*Rhus pentaphylla*): a grey bark used in the north of Africa for dyeing and tanning. Egyptian sumac (*Rhus oniyacantha*) grows in Egypt and Asia Minor. The bark of the root is employed in tanning. *Rhus lucida*, shining-leaved sumac, *Rhus thunbergi*, *Rhus levigata* and *viminialis* are produced at the Cape. *Rhus rhodanthema* (Queensland sumac) and *Rhus elegans* (also from Australia) are used in dyeing and tanning.

Experimental Researches on the Electrolytic Preparation of Sodium and Aluminium.—A. J. Rogers.—(From the CHEMICAL NEWS).

Metallurgical Use of Aluminium and Ferro-aluminium (*Dingler's Polytech. Journal*).—G. Arth.—An account of the use of aluminium in increasing the fluidity of melted iron and preventing blow-holes. Its addition to the melted iron in the converter cannot be recommended on account of the increased expense. A 10-ton Bessemer charge with an addition of 0.1 per cent aluminium will come to 956 francs.

Working Aluminium.—From the *Scientific American*.

The Properties of Aluminium.—A. E. Hunt, J. W. Langley, and C. M. Hall.—From the *Journal of Chemical Industry*.

Tempering and Hardening Steel for Cannon and Projectiles.—Prof. Watson Smith.—From the *Journ. Soc. Chem. Industry*.

On Double Explosions in Puddling Furnaces.—Haeckle (*Stahl und Eisen*).—The author considers that the first of these twin explosions is due to the sudden evaporation of a large quantity of water in consequence of the cessation of the spheroidal state. This first explosion is followed by a partial vacuum in the interior of the apparatus, when there ensues a simultaneous aspiration of air, and of the combustible gases of the furnace,—carbon monoxide and hydrocarbons. This detonating mixture is ignited in contact with the hot walls of the furnace and causes the second explosion.

Practical Researches on Zincing.—B. Preu (*Chem. Zeitung*).—Of three known methods the author prefers one in which the bath is composed simply of zinc, covered entirely or in part with a layer which prevents oxidation. Sal-ammoniac gives the best results, but it evaporates rapidly and has to be renewed frequently. It diminishes the dangers of explosion, but it occasions unpleasant vapours.

Glass and Ceramic Art.—Under this head come accounts of Japanese enamels (*Chemiker Zeitung*), photographic process for decorations in relief (*Sprechsaal*), manufacture of marbled glass (*Sprechsaal*), yellow lining glass, by Hananek (*Sprechsaal*), new red glass (*Scientific American*), enamels free from lead (*Chemiker Zeitung*).

On Horse-Fat.—L. Lenz (*Chemiker Zeitung*).—Fresh horse-fat, if melted in the water-bath, is yellow and neutral; it has the consistence of butter, and after a few days it becomes viscid. Its weight remains constant for four weeks, then it gained 0.691 grm. in the first year and 0.201 in the second, after which its weight remained constant. The original weight of the sample was 22.521 grms.

Oxidation of Gallic Acid, of Tannin, and of the Tannic Acids of the Oak.—Dr. C. Böttger.—The author on studying the action of nitric acid upon tannin and gallic acid, obtained along with oxalic acid a smaller quantity of two other acids, which may be separated by means of their calcium salts.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. vi., Nos. 4 and 5, September 5, 1891.

On Azothydric Acid.—E. Noetting and E. Grandmoulin.—According to the researches of Curtius, diazobenzolamide may be considered as the phenylic ether of azothydric acid. This derivative may easily be prepared by diazotising dinitraniline, transforming it into perbromide, and treating the latter with ammonia. Under the influence of alcoholic potassa it is split up very sharply, yielding potassium salts of dinitrophenol and azothydric acid. On acidifying and distilling there passes over an aqueous solution of azothydric acid, which is identified by means of the characteristic reactions described by Curtius. The authors intend to study the other nitrised diazobenzolamides, and to ascertain the most favourable conditions for the preparation of azothydric acid.

Boron Selenide.—Paul Sabatier.—The author obtains boron selenide by passing a current of very dry hydrogen selenide over amorphous boron, kept at a red heat in a tube of Bohemian glass. The boron is entirely transformed into a yellowish grey selenide, showing no trace of fusion. Beyond the "boat" the sides of the tube are lined with a thin powdery layer of pale yellow boron selenide; further on there are found small drops of vitreous selenium, then of scarlet selenium mixed with a little selenide. The sublimate of yellow selenide is briskly destroyed by water, yielding boric acid and hydrogen selenide. The composition of the selenide is B_2Se_3 . A sub-selenide has also been obtained, Bo_4Se . Boric selenide is much less volatile than boron sulphide and even than selenium.

Silicon Selenide.—Paul Sabatier.—This compound was obtained by heating crystalline silicon to redness in a current of dry hydrogen selenide. The conversion takes place without incandescence. The selenide takes the form of a melted, hard, incandescent body of a metallic appearance, which does not appear volatile at the temperature of the experiment. Its composition is $SiSe_2$. Water acts upon it briskly, yielding silica and hydrogen selenide.

Action of Ammonia upon Mercury Cyanide and its Compounds with Haloid Salts.—Raoul Varet.—This paper has been already noticed.

Researches on Lead Chromate.—MM. Lachaud and Lepierre.—Also previously noticed.

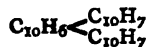
Researches on Thallium.—M. Lachaud and C. Lepierre.—The authors describe a series of experiments on thallium chromate prepared by precipitating pure thallous sulphate with neutral potassium chromate. The salt obtained, Tl_2CrO_4 , is amorphous and of a lemon-yellow colour. It was treated successively with dilute potassa, concentrated potassa, potassa in a state of fusion, and potassium nitrate. They have also obtained thallium chlorochromate, but not in a state of perfect purity. Reference is made to a new method of determining thallium which is to furnish the subject of future communication.

Determination of Chrome Yellows.—The method proposed by the authors will be given in full.

Molecular Lowering of Phenol.—MM. Juillard and Curchod.—The authors find that the molecular lowering of synthetic phenol, fusible at 41.2° , varies with the nature of the substance dissolved. The mean value is 68.5 for water, β -naphthol, paratoluidine, aniline, nitrobenzene, phthalic anhydride, diphenic anhydride, α -naphthylamine, amyl alcohol, vicinic acid, and anhydrosulphuric carbonic acid. For the neutral ethers, especially the ethers of the bibasic acids, the mean is 75.81 . The value 68.5 is the most general experimental lowering, and must consequently be adapted for cryoscopic experiments made with phenol.

Boron Sulphides.—Paul Sabatier.—The action of hydrogen sulphide upon boron heated to redness yields not merely normal boron sulphide, B_2S_3 , but also a borous sulphide, B_4S_5 , and a small proportion of a hydrosulphate which is doubtless $B(SH)_3$.

On Picene.—R. Lespieau.—The author finds that the carbide described by M. Roux as—



is the picene described by Burg.

Variations of the Colour of Cobalt Chloride.—M. Engel.—This extensive memoir does not admit of useful abstraction.

Researches on the Sulphonic Derivatives formed by the Action of Sulphuric Acid upon Castor Oil.—M. Scheurer-Kestner.—Alizarin oil (oil for reds) is a complex compound, including polymerised fatty acids and sulphones, partly normal and partly desulphonised by the action of the washing waters. The sulphonic acids are present in the state of hydrates. A yellowish "raising" (*avisage*) is occasioned by the sulphonic acids, and a bluish one by acids which are desulphonised but polymerised.

Methæmoglobine derived from Oxycarbonic Hæmoglobine.—H. Bertin-Sans and J. Moitessier.—From the experiments of the authors it may be concluded that the solutions of methæmoglobine obtained by means of oxycarbonic hæmoglobine, or by treating oxygenated hæmoglobine with a current of carbon monoxide, contains simply methæmoglobine and carbon monoxide in solution. If by the action of ammonium sulphide these solutions give oxycarbonic hæmoglobine, it is because the methæmoglobine is transformed into hæmoglobine, which is combined with dissolved carbon monoxide. The authors will shortly publish a process for detecting small quantities of carbon monoxide in blood.

Certain Coloured Reactions of the Carbohydrates.—G. Bertrand.—If we heat gently a glucose with concentrated hydrochloric acid holding in solution a small quantity of phloroglucine (one or two drops of a saturated aqueous solution of this substance to some c.c. of acid), there appears a yellow colour which rapidly passes to an orange-red. On continuing to heat there is formed a dirty red precipitate, and the liquor is partly decolourised. This reaction is produced also in the cold, but it then requires several hours. The author finds that the red colouration mentioned above is obtained with all the glucoses and with bodies capable of forming such on hydration. But the hydrochloric acid must be strong, about 1:18. With orcin and hydrochloric acid an orange-red liquid is yielded by Soxhlet's glucose, the glucose of cellulose, galactose, mannose, levulose, sorbine, saccharose, lactose, maltose, raffinose, melizitose, stachyose, trehalose, isodulcitol, glycogene, inuline, levuline, potato-starch, rice-starch, dextrine (commercial), achroodextrine, amygdaline, salicine, hesperidine. The following give a violet-blue liquid:—Arabinose, xylose, cherry-gum, strow-gum, gum of pines, gums arabic and senegal (the two latter a violet red). The following yield no colouration:—Xylite, sorbite, dulcitol, mannitol, perseitol, inositol, penitol, berginitol, Peligot's saccharine.

The Acidity of Green Grapes and the Preparation of Malic Acid.—Ch. Ordonneau.—Unripe grapes and grapes from certain climates (*e.g.*, Vendée) contain much malic acid. Wine from Vendée yielded in 1890 more than 15 grms. of tartro-malate per litre. In certain white wines malic acid is present in greater quantity than the total tartaric acid. The author proposes to obtain malic acid from the dregs remaining on distilling wines.

The Hydrates of Cobalt Chloride and the Changes of Colour of this Compound.—A. Potilitzine.—The author considers that the changes of colour depend on the dissociation of a hydrated salt, or on the elimination of water.

MEETINGS FOR THE WEEK.

- MONDAY, 7th.—Society of Arts, 8. "The Pigments and Vehicles of the Old Masters," by A. P. Laurie, M.A.
— Royal Institution, 5. General Monthly Meeting.
— Society of Chemical Industry, 8. "A Contribution to our Knowledge of the Soluble and Resinous Constituents of Bituminous Coals," by Watson Smith, F.C.S. "The Salt Industry of India," by Dr. Murray Thomson.
WEDNESDAY, 9th.—Society of Arts, 8. "The World's Columbian Exposition at Chicago in 1893," by Mr. James Dredge.
— Geological, 8.

TO CORRESPONDENTS.

T. Veasey.—We do not see how such a thing is possible without interfering with its useful qualities.

ENGLISH TRANSLATION OF MENDELEEF'S CHEMISTRY.

The Principles of Chemistry.

By D. MENDELEEF,

Professor of Chemistry in the University of St. Petersburg.

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THE CHEMICAL NEWS.

Vol. LXIV., No. 1672.

A CALCIUM PHOSPHATE DEPOSITED FROM AN ACETIC ACID SOLUTION.

By HERBERT E. DAVIES, B.A., B.Sc.

If the precipitate obtained by adding ammonia to a hydrochloric acid solution of tri-calcium phosphate be dissolved in acetic acid, and the solution kept for some days, crystals begin to deposit and continue to do so for some time.

Having obtained about 2 grms. of these crystals, I washed them thoroughly with water and then dried them in vacuo over sulphuric acid for about four days. They then appeared as brightly glittering prismatic crystals.

On heating them in the water-oven for several hours they only lost weight to a very slight extent (0.85 per cent), and prolonged heating to a bright redness in the muffle was necessary before they ceased to lose weight.

Analysis of the crystals as dried over sulphuric acid gave the following result:—

Ca	..	..	..	32.86
P	..	..	..	18.08
O	..	..	..	56.06
H	..	..	..	2.94

99.94

From this the formula CaH_3PO_6 is calculated. A substance having the same percentage composition is described by Groves as being formed when Na_2HPO_4 is added, drop by drop, to an excess of CaCl_2 , but its properties, as described by him, differ from those of the compound prepared as above.

From the fact that there is practically no loss of water when heated to 100°C ., and, further, that there is no definite temperature at which two molecules of water are lost, together with the fact that a large proportion of the loss occurs only at a very high temperature, it seems probable that the compound does not contain water of crystallisation. If this be so it seems as though the compound were a derivative of the maximum hydroxide of phosphorus $\text{P}(\text{OH})_4$. If we suppose this to react with the hydroxide of calcium, $\text{Ca}(\text{OH})_2$, and one molecule of water to be lost we get—



as the formula of the body.

The Royal Institution Laboratory,
Liverpool.

ON CHEMISM IN LIVING PROTOPLASM.

By Prof. W. PREYER and G. WENDT (of Berlin).

(Continued from p. 275).

THE assimilation and dissimilation of matter, both constantly manifested in living protoplasm can be nothing other than chemical processes, since true transmutations of matter, i.e., chemical combinations externally and internally different, can be produced only by atomic reactions. Otherwise the very foundations of chemical science would be insecure.

The first five of the six essentials—attendant phenomena of every chemical reaction—have been directly

observed or experimentally demonstrated as the fundamental functions of protoplasm; but not the sixth—the chemical action of mass.

On the basis of his experiments on the dead space in chemical reactions, Liebreich concludes that "the occurrence of every chemical reaction is possible only in excess of a certain definite magnitude of the space in which it is to ensue." It cannot be denied that in capillary spaces the physical influence of the enclosing sides and the various tension of the liquid surfaces are magnitudes which must be carefully taken into account. Almost all capillary reactions, as it is well known, are exceedingly sensitive. It has long ago been decided that these values, which may be neglected under ordinary circumstances, are very considerably modified on quite minute alterations of spacial relations, of the surface of the sides, the physical properties of the liquids concerned, and on the slightest impurities or admixtures; as also on very trifling modifications of temperature, or illumination, &c. Hence it is intelligible that in such variations, which seem quite insignificant for the conditions of the laboratory, important alterations must ensue in capillary reactions. Hence the exact repetition of such experiments becomes an exceedingly difficult problem. Even an exact statement of the conditions of an experiment is often almost impossible.

In consequence of this conclusion an ordinary chemical reaction can scarcely be imagined in a microscopic test-tube, in a microscopic retort, or in a microscopic flask. Liebreich says very briefly that "a certain size" of the cell spaces is needed if a quite different, and in a manner degenerate, chemical process is not to ensue.

What is to some extent a degenerate chemical process is not intelligible, but in any case our assumption, which agrees perfectly with the first words, appears admissible, namely, that in microscopical protoplasm there are always spaces where a chemical action of mass does not reach validity in opposition to very strong physical influences, though nevertheless intense chemical reactions take place. But where there is no chemical action of mass in protoplasm, the effort towards chemical equilibrium cannot be present. The important formula of Guldberg and Waage— $k_1 p_1 q_1 = k_2 p_2 q_2$, the law of the chemical action of mass—which is not only inductively derived by experiment, but also deductively from the mechanical theory of heat, does not then hold good for the specific chemism of protoplasm.

This law may be most briefly expressed as follows:—

If p_1 and p_2 signify the relative quantities of the free bases, and q_1 and q_2 the quantities of the two salts formed in molecular weights, and k_1 and k_2 constants depending on the mutual affinities of the bases and the salts to each other, the energy with which the two antagonistic reactions tend to be effected may be expressed by $k_1 p_1 q_1$ and $k_2 p_2 q_2$. The main law of the chemical action of mass is then expressed by the formula $k_1 q_1 q_2 = k_2 p_2 q_1$,—that is, each of the two antagonistic reactions tend to be carried out with an intensity proportional to the relative quantity of the matters concerned or to the number of their mols., and equilibrium is reached at that proportion of quantities at which the opposing forces become equally great.

That this law cannot hold good for living protoplasm follows from the microscopic smallness of the protoplasmic tissues, which display the most intense metabolism, and the unparalleled variability of protoplasmic matter.

However different are the opinions of the best observers as regards the nature of protoplasm, all, doubtless, agree that protoplasm, whether it is found in the Amœba living freely in the water, or in the Leucocytes circulating in the plasma of the blood in the sluggish corpuscles of conjunctive tissue, or in the briskly moving cholera bacillus, or in the nucleus of an ovum, in a ganglionic globule, or in a glandular cell, is extremely complicated, and not, as was formerly supposed, homogeneous; not a mucoid, an albumenoid, nor indeed a matter of whatever kind, but that it is exactly characterised by its changes of material, of forces, and of form.

Protoplasm is no chemical compound (to aim at proving this would, in our day, be mere trifling); it is also no simple mixture of chemical compounds as long as it breathes, assimilates, moves, and develops; for we do not call a working machine a simple mixture of the combinations or elements of which it is constructed, or which it takes in and gives out. It is also no mixture of chemical compounds, for we easily recognise for the most part in protoplasm heterogeneous parts, independent of the nucleus of the vacuolæ, and of differentiated appended structures. It is altogether no structure which, on mechanical or ultimate analysis, yields constant relative quantities of the substances which pre-exist in it, or which may be obtained from it, carbon, nitrogen, hydrogen, phosphorus, sulphur, calcium, &c., but it has an inconstant composition.

(To be continued).

THE BEHAVIOUR OF AZOIMIDE WITH LIVING ORGANISMS.*

By O. LOEW.

(Continued from p. 276.)

WHEN 1 grm. of scraped meat was placed in a flask and covered with 20 c.c. of a 1 per cent solution of sodium azoimide, it remained unchanged, and did not putrefy even if infected with schizomycetes. In a check flask, offensive putrefaction set in after twenty-four hours, effected by a multitude of bacteria in brisk movement.

4. Experiments with *Hyphomycetes*.

To 50 c.c. of a cultivation liquid of the same composition as that used in the experiments with bacteria, there was added, beside 1 part per 1000 sodium azoimide, 2 parts per 1000 mono-potassium phosphate, and the liquid was then infected with the spores of *Penicillium* and *Aspergillus*. But even after some weeks not a trace of the mycelium of mould was developed, even if diammonium phosphate was present in addition to sodium azoimide.

Another nutrient solution, which instead of a tartrate contained 5 parts per 1000 of glucose, and also 0.5 per 1000 of sodium azoimide, developed even after many weeks not a trace of the filaments of mould, in spite of infection and exposure to the air. A check specimen, which contained nitrogen in the form of 0.5 per 1000 ammonium chloride, developed on the third day a thin film of mould along with a bacterial turbidity, and on the eighth day a considerable layer of mould.

5. Experiment with *Saccharomycetes*.

A portion of pressed yeast of the size of a pea was shaken up with 10 c.c. of water; one half of the liquid was mixed with 5 parts per 1000 of sodium azoimide, and the other was let stand for two days without this addition. The latter portion had already an offensive smell, and the supernatant liquid contained numerous bacilli; the former was inodorous and free from bacilli. The yeast which had settled to the bottom was brought in contact in a narrow tube with about 5 c.c. solution of glucose. In both cases fermentation was set up in about 25–30 minutes, though less briskly in the portion which had been treated with sodium azoimide.

Saccharomycetes are, therefore, more resistant than *schizomycetes* and *hypomycetes*, as has been already shown in many other cases. Whether the poison here penetrates less readily or whether protective arrangements exist in the protoplasm remains for the present undecided.

6. Experiments with *Infusoria*.

If a drop of a 1 per cent solution of sodium azoimide

is brought in contact with infusoria under the microscope, there is a sudden cessation of all vital movements. A 0.1 per cent solution in spring water does not cause the movements to cease in less than 2–2½ hours. In the *Vorticellæ* there sets in firstly partial paralysis, when the stem and the cilia become rigid. In *Stylomychia* the movements become for a short time very violent before they cease altogether. Other *Infusoria* contract to motionless globules, whilst the *Euglenæ* twist backwards and forwards for some time before life ceases. If, accidentally, species of *Cyclops* (belonging to the *Crustacea*) are found among the infusoria, their rapid movements are quickly paralysed until life is entirely extinguished.

If the solution is diluted with 10 parts of water, living *Vorticellæ* and *Amœbæ* may be observed even after twelve days.

7. Experiments on Various Aquatic Animals.

In a 0.5 per mille solution of sodium azoimide in well water, *Nematodes*, *Planariæ*, *Ostracodæ*, *Copepods*, wood lice, small insect larvæ, and young snails (*Planorbis*, *Limnæa*) die in 30–40 minutes. In 2½–3 hours small water-beetles die; leeches later.

In a 0.1 per 1000 solution *Crustaceans* die in 20–24 hours, death being preceded by paralysis. Water-beetles and snails die after four days; leeches and insect larvæ were still living after six days.

8. Experiments on *Mammalia*.

Prof. Emmerich, of the Hygienic Institute, here kindly made a few experiments, and reports as follows:—

"Your conjecture concerning the action of sodium azoimide is fully confirmed. The subcutaneous injection of 1 c.c. of the 1 per cent solution caused in a large mouse in ten seconds sudden cramps, emprosthotonus, and instant death. Even 0.1 c.c. injected into a mouse subcutaneously occasioned in three minutes cramp of the diaphragm, and within four minutes paralysis of the extremities. In two minutes more there set in clonic cramps of all the muscles, emprosthotonus, and death. On the immediate opening of the thorax, the auricles contracted a few times, and the heart then became still. The blood was very dark."

(To be continued).

DETERMINATION OF SMALL QUANTITIES OF ALKALI AND RECOGNITION OF THE NEUTRALITY OF WATER.

By F. MYLIUS and F. FOERSTER.

(Concluded from p. 277).

THE figures signify thousandths of a m.grm., and show that the factor ascertained for soda is sufficiently accurate for potassa and ammonia. From all this it follows that our colorimetric method suffices to determine even 0.005 alkali with some accuracy.

For the appreciation of the colorimetric method as well as for that of titration with mille-normal solutions, we require a knowledge of the influence of carbonic acid upon the determination of very small quantities of alkali, the more so as our experiments for the determination of the empirical factor above mentioned were made with a solution of sodium carbonate instead of with one of pure sodium hydroxide. "Neutral" water was therefore saturated with carbonic acid obtained by heating sodium bicarbonate. A saturated solution of carbonic acid contains about 0.9 grm. carbonic acid per litre. This solution was mixed in various proportions with neutral water, and known quantities of soda were added to the mixture. The red colour obtained in the solutions of alkali thus obtained, after shaking out with ethereal solution of eosine and with aqueous ether, was determined. The results were as

follows:—In presence of 0.05 m.grm. Na_2O in 100 c.c. water, which had required 55 c.c. of the alkaline solution of eosine, there were found on the simultaneous presence of—

9.7 equivs. CO_2		52.3 c.c. solution of eosine.		
16.0 "		49.0 "	"	"
27.0 "		42.8 "	"	"
128.0 "		27.3 "	"	"

We see that, as it might have been expected, the influence of carbonic acid when in large excess is very considerable, whilst a moderate excess is of little importance. We shall not be deceived if we assume that the small possible fluctuations of the quantity of carbonic acid always present in water, as they are produced by the use of solutions of sodium carbonate instead of soda-lye, have scarcely any influence upon our colorimetric determinations of alkali. This result was to be anticipated in view of the large excess of eosine always present in the determinations, and of the above mentioned indifference of carbonic acid on titration with dilute solutions, using very small quantities of iodeosine. The fact that the figures referring to ammonia in the above conspectus show the same agreement as those referring to potassium and sodium carbonate agrees with what has been above mentioned.

A few instances may be given to show the applicability of the colorimetric method. With its aid the determination of ammonia can be effected with some degree of accuracy even in dilutions in which Nessler's reagent scarcely admits of a qualitative conclusion as to the presence of ammonia. When distilled water from Kahlbaum (a dealer in pure reagents) was distilled with soda, each 100 c.c. of three successive portions of the distillate represented 10 c.c. of the eosine solution, which would correspond to 0.0274 m.grm. ammonia per litre of the distillate.

The colorimetric method for the determination of alkali permits by reason of its great sensitiveness a determination of the quantities of alkali extracted by aqueous liquids from glass vessels in which they have been kept. We mention a series of experiments in order to show the changes which water undergoes when kept in a glass bottle. The bottle held about 1 litre, and consisted of good glass; it had been well rinsed out with water before the experiments. When neutral water was kept in it for some time, successive portions of the water of 100 c.c. each showed the following values:—

1 day, 15 c.c. solution of eosine	=	0.0094 Na_2O .
3 " 21.5 "	"	= 0.017 "
8 " 32.3 "	"	= 0.027 "

The method of determining alkali which we have here proposed may be used for the determination of the alkaline earths in the same manner as for the alkalies. As it is easily seen, small quantities of mineral acids may be also determined colorimetrically if we make use of alkaline solutions of known strength according to the practice of volumetric analysis. A somewhat wide field is therefore open for the applicability of the method. It may also be occasionally useful in the examination of animal and vegetable liquids as also in the investigation of minerals. In this direction an experiment may be mentioned which was executed to observe the decomposability of potassic feldspar by water. 5 grms. of coarsely powdered orthoclase prepared by picking, sifting, and repeatedly washing away the adhering dust, were left for forty-eight hours in contact with 100 c.c. of neutral water at a common temperature in a platinum flask. At the end of this time 0.018 m.grm. potassa (K_2O) had passed into solution, as it was concluded from the intensity of the colour on examination.—*Berichte der Deutsch. Chem. Gesell.*, vol. xxiv., p. 1482.

NINTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

THE Committee on Indexing Chemical Literature respectfully presents to the Chemical Section its ninth annual report.

Since our last meeting the following bibliographies have been printed:—

1. "A Bibliography of Geometrical Isomerism." Accompanying an address on this subject to the Chemical Section of the American Association for the Advancement of Science at Indianapolis, August, 1890, by Prof. Robert B. Warder, Vice-President. *Proc. A. A. A. S.*, vol. xxxix., Salem, 1890. 8vo.

2. "A Bibliography of the Chemical Influence of Light," by Alfred Tuckermann. Smithsonian Miscellaneous Collections, No. 785, Washington, D.C., 1891. pp. 22, 8vo.

3. "A Bibliography of Analytical Chemistry for the Year 1890," by H. Carrington Bolton. *Four. Anal. Appl. Chem.*, v., No. 3. March, 1891.

We chronicle the publication of the following important bibliography.

"A Guide to the Literature of Sugar." A book of reference for chemists, botanists, librarians, manufacturers, and planters, with comprehensive subject-index. By H. Ling Roth. London: Kegan Paul, Trench, Trübner, and Co., 1890. 8vo., pp. xvi.—159.

This work contains more than 1200 titles of books, pamphlets, and papers relating to sugar. Many of the titles are supplemented with brief abstracts. The alphabetical author-catalogue is followed by a chronological table and an analytical subject-index. The compilation extends to the beginning of the year 1885, and the author promises a supplement and possibly an annual guide.

This ambitious work is useful but very incomplete; it does not include glucose. The author gives a list of fifteen periodicals devoted to sugar, and omits exactly fifteen more recorded in Bolton's *Catalogue of Scientific and Technical Periodicals* (1665—1882). (Washington, 1885.) Angelo Sala's *Saccharologia* (Rostock, 1637), is not named, though mentioned in Roscoe and Schorlemmer and elsewhere. Notwithstanding some blemishes, this work is indispensable to chemists desirous of becoming familiar with the literature of sugar. It is to be hoped that a second edition brought down to date may be issued by the author.

4. "A Bibliography of Ptomaines" accompanies Prof. Victor C. Vaughan's work. "Ptomaines and Leucomaines," Philadelphia, 1888. (Pages 296—314). 8vo.

Chemists will hail with pleasure the announcement that a new "Dictionary of Solubilities" is in progress by a competent hand. Prof. Arthur M. Comey, of Tuft's College, College Hill, Mass., writes that the work he has undertaken will be as complete as possible. "The very old matter, which forms so large a part of Storer's Dictionary, will be referred to, and in important cases fully given. Abbreviations will be freely used, and formulæ will be given, instead of the chemical names of substances, in the body of the book. This is found to be absolutely necessary, in order to bring the work into a convenient size for use. . . . The arrangement will be strictly alphabetical. References to original papers will be given in all cases. . . ."

Professor Comey estimates his work will contain over 70,000 entries, and will make a volume of 1500 to 1700 pages.

The following letter from Mr. Howard L. Prince, Librarian of the U.S. Patent Office, explains itself.

* From advance proof-sheets of the *Proceedings of the American Association for the Advancement of Science*, Washington Meeting, 1891.

UNITED STATES PATENT OFFICE,
Washington, D.C., February 11, 1891.

DR. H. CARRINGTON BOLTON, University Club, N.Y.

DEAR SIR,—In response to your request I take pleasure in giving you the following information regarding the past accomplishments and plans for the future of the Scientific Library in the matter of technological indexing.

The work of indexing periodicals has been carried on in the Library for some years in a somewhat desultory fashion, taking up one journal after another, the object being, apparently, more to supply clerks with work than the pursuance of any well-defined plan. However, one important work has been substantially completed, viz., a general index to the whole set of the *Scientific American* and Supplement from 1846 to date.

It is unnecessary for me to point out to you the importance of this work, embracing a collection which has held the leading place in the line of general information on invention and progress, the labour of compiling which has been so formidable that no movement in that direction has been attempted by the publishers, except in regard to the supplement only, and that very imperfectly. This index embraces now 184,000 cards, not punched, and at present stored in shallow drawers and fastened by rubber bands, and, of course, they are at present unavailable for use. There is little prospect of printing this index, and I have been endeavouring for some time to throw the index open to the public by punching the cards and fastening them with guard rods, but as yet have made no perceptible impression upon the authorities, although the expense of preparation would be only about 70.00 dollars.

There has also been completed an index to the English journal *Engineering*, comprising 84,000 cards, from the beginning to date.

An index to *Dingler's Polyt. Jour.* was also commenced as long ago as 1878, carried on for six or seven years and then dropped. I hope, however, at no remote date, to bring this forward to the present time.

On taking charge of the library I was at once impressed with the immense value of the periodical literature on our shelves, and the great importance of making it more readily accessible, and have had in contemplation for some time the beginning of a card index to all our periodicals on the same general plan as that of Rieth's Repertorium. I have, however, been unable to obtain sufficient force to cover the whole ground, but have selected about 150 journals, notably those upon the subjects of chemistry, electricity, and engineering, both in English and foreign languages, the indexing of which has been in progress since the 1st of January. This number includes substantially all the valuable material in our possession in the English language, not only journals, but transactions of societies, all the electrical journals, and nearly all the chemical in foreign languages. This index will be kept open to the public as soon as sufficient material has accumulated. In general plan it will be alphabetical, following very nearly the arrangement of the periodical portion of the Surgeon-General's catalogue. I shall depart from the strictly alphabetical plan sufficiently to group under such important subjects as chemistry, electricity, engineering, railroads, &c., all the subdivisions of the art, so that the electrical investigator, for instance, will not be obliged to travel from one end of the alphabet to the other to find the divisions of generators, conductors, dynamos, telephones, telegraphs, &c., and in the grouping of the classes of applied science the office classification of inventions will, as a rule, be adhered to, the subdivisions being, of course, arranged in alphabetical order under their general head, and the title of the several articles also arranged alphabetically by authors or principal words.

With many thanks for the kind interest and valuable information afforded me, I remain,

Very truly yours,

HOWARD L. PRINCE,
Librarian Scientific Library.

The committee much prefers to record completed work than to mention projects, as the latter sometimes fail. It is satisfactory, however, to announce that the indefatigable indexer, Dr. Alfred Tuckerman, is engaged on an extensive "Bibliography of Mineral Waters." The Chairman of the Committee expects to complete the MS. of a "Select Bibliography of Chemistry" during the year, visiting the chief libraries of Europe for the purpose this summer.

H. CARRINGTON BOLTON, *Chairman*.

F. W. CLARKE.

ALBERT R. LEEDS.

ALEXIS A. JULIEN.

JOHN W. LANGLEY.

ALBERT B. PRESCOTT.

(Dr. Alfred Tuckerman was added to the committee at the Washington Meeting to fill the vacancy).

ON THE OCCURRENCE OF NITROGEN IN URANINITE, AND ON THE COMPOSITION OF URANINITE IN GENERAL.*

By W. F. HILLEBRAND.

(Continued from p. 281.)

In the following table all the foregoing analyses of Norwegian material have been re-calculated to the percentages found, excluding the insoluble matter, in order that their true relations may appear at a glance, whereby the sum of the rare earths combined is given instead of each earth or group of earths by itself. Only those constituents are tabulated which may be considered unquestionably in whole or in part as belonging to the uranium mineral. Silica, ferric or ferrous oxide as it may be, the small amounts of magnesia, alkalies, &c., may be thrown out as derived from admixed impurities. Lime from its close relationship to the other earths has been retained, though it is undoubtedly, in part at least, derived from foreign silicates.

TABLE V.—Analyses of Norwegian Uraninite
Re-calculated.

	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.
UO ₃ ..	32.04	25.48	26.04	32.50	35.69	42.11	27.12
UO ₂ ..	48.25	50.97	50.83	44.57	43.56	24.51	44.71
Earths	7.97	10.18	9.96	10.64	8.12	13.57	14.03
PbO..	9.45	10.11	10.14	9.61	9.48	10.66	11.08
CaO..	0.39	0.77	0.45	0.36	0.41	1.07	0.62
H ₂ O..	0.77	0.73 (a)	0.87	0.78	0.79	1.23	?
N ..	1.23	1.28	1.28	1.05	1.08	?	1.26

(a) A portion of this water was perhaps derived from the large amount of foreign matter contaminating the uraninite.

An examination of analyses XII. to XVI. as re-calculated above hardly allows of any other conclusion than that the specimens from the above four different quarries about Moss belong to one and the same mineral species. While analysis XII. differs in some respects from Blomstrand's analysis of bröggerite, which is here reproduced in its original form and as modified by substitution of Fe₂O₃ for FeO, it simply serves to show, assuming correct analyses, that the mineral may vary in composition in the same quarry, for, as before mentioned, this is the original material from which Blomstrand made the species.

The estimation of UO₃ in the analyses of Table IV. is thoroughly to be depended on, aside from the slight deduction to be made for possible ferrous oxide, while in

* From "Bulletin No. 78, U.S. Geological Survey, 1889-90." An abstract of this paper was published in the *Am. Jour. Sci.*, vol. 21, p. 384.

Blomstrand's Bröggerite.

UO ₃		38.82	36.31
UO ₂		41.25	43.62
ThO ₂		5.64	5.64
Y ₂ O ₃		2.42	2.42
Ce ₂ O ₃		0.38	0.38
CaO		0.30	0.30
PbO		8.41	8.41
FeO		1.26	Fe ₂ O ₃ 1.40
H ₂ O		0.83	0.83
SiO ₂		0.81	0.81
		100.12	100.12

view of the want of evidence as to the manner of filling his tubes with carbonic acid there is no guarantee that Blomstrand's figure may not be too low. Leaving out of consideration for the moment the nitrogen, it is clear in any case that the formula evolved by him from his analysis cannot be derived from No. XII.

In regard to analyses XIII. and XIV., there can exist no doubt whatever as to the identity of the material derived from Profs. Brögger and Nordenskiöld independently. A comparison of them with Lorenzen's analysis, coupled with the fact that not one of the specimens from the neighbourhood of Moss above analysed contains less than 8 per cent of earths, gives rise to the strongest possible suspicion that that analyst has overlooked thorium altogether, notwithstanding the fact that the present material is from Elvestad and Lorenzen's (*Nat. Mag. f. Naturv.*, vol. xxviii., p. 249) was from Huggenäsken.

Lorenzen's Uraninite.

UO ₃		38.23	37.73
UO ₂		50.42	50.89
PbO		9.72	9.72
FeO		0.25	Fe ₂ O ₃ 0.28
CaO		0.21	0.21
H ₂ O		0.70	0.70
SiO ₂		0.31	0.31
		99.84	99.84

Prof. Brögger, as quoted (*ante*), says, however, that the material sent by him is to the best of his knowledge from the same place as that analysed by Lorenzen, and this appears probable from the fact that the specimens from Huggenäsken sent by Prof. Nordenskiöld show a totally different ratio between UO₂ and UO₃ (anal. XVI.). If it should prove that Lorenzen erred in overlooking thorium, another of Blomstrand's supports in favour of the orthouranate formula for all uraninites, including bröggerite and cleveite, is knocked away, the first being the earlier and, as shown, incorrect analysis of Branchville uraninite.

The oxygen ratios calculated for analyses XII. to XVI., counting all earths as thorium, whereby the comparison is very little affected, since the percentages of the other earths are almost alike in all analyses, are as given below, as also the ratios for Blomstrand's bröggerite calculated from the second column (see above) instead of the first in order to compare properly with the others.

It is seen that none of the analyses conform even approximately to the ratio for Blomstrand's, except that of the mineral from Huggenäsken. A re-calculation of all on the basis of FeO for Fe₂O₃ and consequent changes in UO₂ and UO₃, and separation of the earths, would give the normal ratio 1:1 for Blomstrand's analysis, but

the others would differ from it more widely than in the above exhibit.

The correctness of the orthouranate formula for bröggerite itself having been invalidated by the difference between his own analysis and anal. XII. above, it is hardly worth while to discuss its applicability to the Bohemian and Saxon uraninites, of which no complete and reliable analyses seem to have been made, except perhaps the single one by Ebelmen in 1843 on Joachimsthal material, which on re-calculation by Blomstrand was found to conform to his view. No more singular example can be furnished of incorrect conclusions founded on seemingly the best of evidence. No blame can attach to Blomstrand, but it can hardly be doubted that had he been able to analyse material from more than one quarry about Moss he would have seen the impossibility of reconciling the discrepancies in composition so as to admit of the application of one general formula.

It is apparent, notwithstanding the deficiency of earths and one or two other discrepancies, that analysis XVII. was really made upon cleveite, as the label indicated. The density, too, corresponds almost exactly with that found by Nordenskiöld (*Geol. Förh.*, 1878, vol. iv., p. 28; *Zeit. f. Kryst.*, vol. iii., p. 201) and Lindström. In the latter's analysis, which is quoted below, "water and a trace of CO₂" are given as loss on ignition, a result which under the circumstances must be considered unreliable.

The same objection applies to Hidden and Mackintosh's analysis of nivenite (*Am. Jour. Sci.*, [3] 1889, vol. xxxviii., p. 481), where it is stated plainly that the water represents loss on ignition. The analyses of cleveite and nivenite are here given together with XVII. from Table IV. for convenient comparison. It may be mentioned that the 23.07 per cent of UO₂ in cleveite is the mean of two results differing by nearly 14 per cent. Taking the higher as more nearly correct than the mean, almost exact agreement with the figures of analysis XVII. for UO₂ and UO₃ is obtained.

	Nivenite.	Cleveite.	XVII.
UO ₃		46.75	41.71
UO ₂		19.89	23.07
ThO ₂		7.57	4.60
Ce ₂ O ₃ , &c...		—	2.25
Y ₂ O ₃ , &c...		11.22	9.99
PbO		10.16	10.92
Fe ₂ O ₃		0.58	1.02
CaO		—	0.86
MgO		—	0.14
SiO ₂		—	—
Ign.		2.54	4.96
Insol.		1.22	2.34
CO ₂ and N?		—	—
	99.93	100.75	100.00
	(a) And alk.		

The appearance of cleveite is at once suggestive of alteration, and, in view of the uncertainty attaching to the water determinations for both nivenite and cleveite, it is probable that they represent nearly the same stage of alteration of the same species. What this species is is pretty clearly indicated by analysis XVIII. of Table IV., where the earths are in about the same proportions and total amounts as in XVII., but the UO₃ and UO₂ stand in a very different ratio. The material for this, as before said, came from Arendal, and presumably from the precise locality of the cleveite of analysis XVII., since the pieces

	Mol. wt.	XII.	XIII. and XIV.	XV.	XVI.	Blomstrand's Bröggerite.
UO ₃		287	5.36	4.31	5.44	6.07
UO ₂		271	5.70	6.01	5.26	5.15
Earths		266	0.96	1.21	1.28	1.02
PbO		223	0.68	0.73	0.69	0.60
			1.37	1.85	1.33	1.11

of felspathic rock containing them were in one package without distinguishing labels, but it was unquestionably fresher. The extreme solubility of this material compared with the other Norwegian uraninites is shared by that of analysis XVII., by cleveite, and by nivenite, and is to be explained probably not so much by advanced decomposition as by the preponderance here of a more soluble yttrium-uranium compound. Whether or not this last Arendal material is the source whence cleveite and its American representative have been derived by alteration, as seems most probable, it is in any event a true uraninite of more basic character than any of the Norwegian thorium uraninites, and consequently conforms still less than those to the orthouranate formula.

Bohemian and Saxon Uraninites.—Nitrogen was carefully sought for in uraninite from Przibram, Joachimsthal, and Johanngeorgenstadt, using the apparatus figured (*ante*). The extremely small bulk of gas finally obtained from all of them, after cleansing with potassium hydrate, measured about 0.2 c.m.³ for Przibram and Joachimsthal, and much less for Johanngeorgenstadt, 1 grm. of mineral having been used. The above volume represents about 0.02 per cent in weight of what can hardly be anything else than nitrogen.

None of the specimens contained zirconia, thoria, or other rare earths. Owing to the uncertainty of being able to determine with any close approach to truth the proportions of UO_2 and UO_3 in the presence of sulphides, and compounds of arsenic and vanadium of unknown degree of oxidation, no quantitative analyses have been carried out, but the attempt will yet be made to solve their composition.

Discussion of Analyses.

Hitherto the analyses have been considered in groups and without special reference to the nitrogen. It has been sought to show on grounds which would be valid even without its presence that the orthouranate formula is capable of no general application to uraninite, and that in the one or two cases where it does seem to apply this agreement is probably accidental. Taking into consideration the low atomic weight of nitrogen as compared with uranium, thorium, and lead, it is plain that it must play an important part in the constitution of the molecule, and that therefore its discovery alone, without other evidence furnished by the analyses, is sufficient to invalidate entirely the practically identical formulæ of Comstock and Blomstrand.

Throughout the whole list of analyses in which nitrogen has been estimated, the most striking feature is the apparent relation between the UO_2 and the nitrogen. This is especially marked in the second table of Norwegian uraninites (Table V.), from which the rule might almost be formulated that, given either nitrogen or UO_2 , the other can be found by simple calculation. The same ratio is not found in the Connecticut varieties, but if the imperfect determination of nitrogen in the Branchville mineral is to be depended on, the rule still holds that the higher the UO_2 the higher likewise is the nitrogen. The Colorado and North Carolina minerals are exceptions, but it should be remembered that the former is amorphous, like the Bohemian, and possesses the further similarity of containing no thoria, though zirconia may take its place, and the North Carolina material is so much altered that its original condition is quite unknown.

In the absence of all positive knowledge whatever as to the rôle which nitrogen plays in the mineral, it would be idle to speculate at present upon the proper position of the latter in mineral classification. Much remains to be done before this question can be elucidated, but the general direction which the work must take can be fairly indicated.

But two explanations seem possible to account for the wide differences in the oxygen ratios for UO_3 and total bases, varying as they do from 1 : 4.37 for the Branchville

material of analysis VI. to 1 : 1 for Blomstrand's bröggerite, and even to a ratio indicating acidity for nivenite. Either all the others are alteration products of a mineral having the composition of the Branchville occurrence, or even of some unknown body entirely free from UO_3 ; or they are mixtures of two or more substances which need not necessarily be isomorphous, for Baumhauer's investigations have shown that even well developed crystals of smaltite and chloanthite are often mechanical mixtures. Fractional solution might throw light on this point, and the following are the results of experimentation :—

I. In one of the nitrogen estimations in Glastonbury uraninite by the original method the operation had to be discontinued before solution was complete. The undissolved residue, amounting after extraction of lead sulphate to 0.1234 grm., was found to contain 71.94 per cent UO_2 , the original percentage having been 59.93.

II. 1.095 grms. were boiled for twelve hours with dilute hydrochloric acid in a flask connected with a reversed condenser. The residue was 0.9193 grm., showing that but 16 per cent had been dissolved, and it contained 64.66 per cent UO_2 . The nitrogen was lost.

III. 2.012 grms., when boiled with the same hydrochloric acid for forty-two hours, afforded a residue of 1.4975, showing solution of 25.5 per cent. Its composition was—

UO_3		16.63	} All U as UO_2 82.52.
UO_2		66.82	
Earths		10.81	
PbO		3.02	
N		2.67	
H_2O		(?)	
Insol.		0.37	

100.32

Here it is seen that the UO_2 has increased, and likewise the nitrogen, both in about the same proportion, but it is not clear why the earths and lead oxide should not show a greater change.

These experiments require repetition and extension to other than the Glastonbury mineral, but so far as they go they indicate that uraninite as we know it is not a single chemical substance, and that, as was to be expected in such case, the portion containing most UO_2 is the least soluble. They are not decisive as between the hypothesis of original mixture and that of mixtures resulting from alteration. In this respect the following observations are of interest :—In dilute hydrochloric acid a large piece of North Carolina uraninite falls wholly to finest powder in course of time, which would hardly happen were it one original substance in process of alteration, unless the change affected every smallest particle of the mineral simultaneously and to the same extent. Hydrofluoric acid speedily covers the faces of a bright crystal of Branchville uraninite with a network of fine cracks visible only under the glass, and soon powder can be rubbed off with the fingers.

Whatever may be the eventual conclusion, it will be found that the small amount of water afforded by all analyses must be carefully considered. Small as this amount is, in consequence of its low molecular weight as opposed to uranium, thorium, and lead, it must play an important part in the mineral as a homogeneous whole or in one of its parts if a mixture. In the latter case it will unquestionably be found to belong to the more soluble component.

It is significant that the two uraninites highest in UO_2 give the lowest water, and while it is true that the Branchville mineral appears to contain more than that from Glastonbury, this may be only apparent, for the former was simply ignited in a current of air, while the latter was fused with sodium carbonate, and it is known that the vapours from both possess an acid reaction, and

in the latter case give an increased weight to the calcium chloride tube when no alkaline carbonate is used. It is important that in all future analyses stress shall be laid upon the utmost accuracy in the water determinations, and if insoluble matter is present, it must be ascertained if possible how much, if any, of the water is to be ascribed to this source.

Before leaving this portion of the subject it is necessary to call attention to one difficulty presented by the analyses for which no satisfactory explanation yet presents itself. In the majority of cases in which all constituents have been estimated, the summation is considerably in excess of 100, and in some cases where only one or two are wanting it is evident that they would, if determined, produce a like result. Although it did not seem possible that this almost constant excess could be due to impurities from reagents, or to want of sufficient care in washing or igniting precipitates, it was determined to make an analysis on Glastonbury material with the utmost possible care, using specially prepared reagents and only platinum vessels and reducing the number of weighings to be used as the basis for the summation to a minimum. This analysis, executed partially in duplicate, is No. V. of Table I., and the excess still appears. It seems as if some one of the weighings must have been uniformly too high, but how this can be is a mystery. Efforts will still be made to find a solution. It cannot be sought in a replacement of oxygen by nitrogen in combination with uranium, like the replacement of oxygen by fluorine in many minerals, for since the nitrogen is freed as a gas by sulphuric acid, it is immaterial, so far as the summation is concerned, whether the proportions of UO_2 and UO_3 as found by titration are correct or not. A certain amount of oxygen has been used, and, assuming its correct determination, it does not alter the result whether this has been employed to oxidise a suboxide of uranium to UO_3 , supposing nitrogen to have replaced a part of the oxygen in UO_2 , or only in oxidising UO_2 to UO_3 . In the former case the actual percentage of UO_3 in the mineral would be increased, but the oxygen consumed would be the same.

In a former notice (*Am. Journ. Sci.*, 1889, [3] vol. xxxviii., p. 329) it was mentioned that a relation appeared to subsist between the nitrogen and the UO_2 , but this statement was based on two experiments which subsequent work showed to be illusory. There is certainly a relation, but not exactly such a one as was then surmised. It was found, namely, on examining the portions used for water determinations (by ignition in dry air without sodium carbonate) for UO_2 and nitrogen, that the residual amounts of these were exactly in proportion to their original percentages, showing that the loss of nitrogen kept step with the oxidation of UO_2 to UO_3 . It was later found that these results were accidental, for by sufficiently long heating the nitrogen was entirely eliminated, so far as the usual tests showed.

(To be continued).

Volumetric Determination of Hydrocarbon Vapours in Coal-gas.—W. Hempel and L. M. Dennis (*Ber. Deutsch. Chem. Gesell.*).—The gas is measured in a simple gas burette over water saturated with coal-gas; it is then conveyed through a capillary tube into a gas pipette, in which it is in contact with 1 c.c. of absolute alcohol over mercury, with which it is shaken up for three minutes. The gas is then returned to the burette, taking care that no alcohol penetrates into the connecting capillary. In order to absorb the alcoholic vapour out of the remaining gas, it is again conveyed into a pipette, in which it is shaken up for three minutes with 1 c.c. of water over mercury, after which the gas is conveyed back into the burette. The difference of volume corresponds to the vapours.

OPENING UP CHROME IRON ORE BY HYDROCHLORIC ACID UNDER PRESSURE.

By PAUL JANNASCH and HANS VOGTHERR.

My recently published method of opening up silicates by means of strong hydrochloric acid under pressure in a special platinum apparatus, has been since applied, in concert with H. Vogtherr, to an extensive series of minerals with great success. We have succeeded in completely opening up silicates, such as garnet (pyrope of Meronitz and Arendal, &c.), also black horn-biende (from Granatilla and from Schima), also cerite, so as to be quite suitable for the purpose of an accurate quantitative analysis.

The more detailed results, as well as the different modifications in the execution of the process, will be published in a future communication. In the present short communication we wish in the first place to direct attention to the energetic action of concentrated hydrochloric acid under pressure upon chrome iron ore, which is well known to be very refractory under the common method of opening up by fusion. It is perfectly opened up by hydrochloric acid at 250°, which will greatly facilitate the accurate and complete analysis of the many important deposits of this mineral. The opening up of the mineral is effected as follows:—

I.—Chrome Iron Ore from Baltimore.

The ore, in fine powder, was mixed with 2 grms. sal-ammoniac and 10 c.c. of hydrochloric acid (4 vols. acid at 1.119 specific gravity to 1 vol. water), sealed up in a tube of potash-glass and heated for 8–10 hours to 275–290°. The acid employed had been previously saturated with ammonium chloride by shaking up with the latter salt. The quantity of ore taken was 1.0426 grms. The silica, = 0.0194 grm. = 1.86 per cent, was volatilised by heating on the water-bath with hydrofluoric and sulphuric acids; the residual sulphuric acid was evaporated on the air-bath, and the residue was ignited and weighed. It amounted to 0.0018 grm. = 0.17 per cent.

II.—Chrome Iron Ore from Frankenstein in Silesia, and III.—Chrome Iron Ore from Orsova.

Both these specimens were treated in a similar manner.

In practice, if it is merely required to determine the percentage of chrome in a specimen, the author's platinum apparatus may be dispensed with, and the opening up may be effected in a sealed tube.—*Ber. d. Deutsch. Chem. Gesell.*, vol. xxiv., p. 3206.

A Spectro-Colorimeter.—D'Arsonval (*Séances Soc. Franc. de Phys.*).—In this instrument the eye-piece of an ordinary Dubosq colorimeter is replaced by a small direct vision spectroscope, the slit of which is fixed vertically to the line separating the two halves of the field of vision. If the liquid under examination is placed in one of the tubes and the standard of comparison in the other, and if the substance produces sufficiently characteristic absorption-phenomena, a given constituent can be recognised even in a mixture of bodies of different colours. The same author describes (*ibidem*) a differential spectrometer without polarisation. The rays coming from the sources of light to be compared are thrown upon two parallel tubes closed by two similar objectives, and placed before a spectrum apparatus. The light of each source is thrown upon one-half of the slit by two pairs each of two total reflective prisms. In order to vary in a measurable manner the luminosity of the two spectra, which appear superimposed, a sliding screen is placed before the two object-glasses, which cuts off the light differently, according to its position.

NEW METHOD FOR THE ANALYSIS OF
TIN ORES, AND FOR THE SEPARATION OF
COPPER AND CADMIUM.*

By J. S. C. WELLS, Ph.D.

TIN ORE.

THE methods for the analysis of tin ores are so tedious and unsatisfactory that I was led, some time ago, to try and discover some simpler way of decomposing the ore; that being the chief difficulty in all the old methods.

In my first experiments, fusing the ore with borax was tried, and although this was found to effect the desired result, as far as the decomposition of the ore, still it introduced other difficulties that caused me to give it up.

The borax, at the high temperature of the fusion, attacked the platinum of the crucible to such an extent that it became necessary to separate the platinum from the tin. Boracic acid, as was to be expected, acted the same as borax. The idea then occurred to me that the ore might possibly be reduced in the same way as the artificial oxide, i.e., by means of nascent hydrogen. On trying the experiment, I found that in this way the tin contained in the ore could easily be obtained in the metallic state. My first tests were made as follows:—About 1 grm. of the finely pulverised ore was placed in a large test-tube with a few pieces of zinc and some dilute hydrochloric acid. The first trials were made on an ore from Cornwall, and it was found to be very easily reduced. A sample of Durango ore, consisting of nearly pure cassiterite, was then tried, but the reduction did not take place as readily as with the ore from Cornwall; the reduction of the latter was nearly complete at the end of an hour, whilst the former at the end of three hours showed little change. I then added a piece of platinum with the zinc and acid, and found the result to be very satisfactory, the ore being quickly reduced. Heating the test to boiling was also found to aid the reaction. The addition of the platinum also facilitates very much the subsequent solution of the reduced tin in hydrochloric acid, tin alone dissolving but slowly in the acid.

It is advisable to shake the test frequently during the reaction, so as to keep the ore in contact with the zinc and platinum. If this is not done, the ore settles to the bottom and the reduction takes place very slowly, if at all.

As soon as the decomposition of the ore appears to be complete, the remaining zinc and the reduced tin are dissolved in hydrochloric acid and filtered from any undecomposed ore or gangue. This residue should again be tested in the same way, with fresh zinc, platinum, and hydrochloric acid, to see if all the tin has been extracted by the first operation. After the tin has been obtained as chloride, it can, of course, be determined by any of the usual methods.

Instead of dissolving in hydrochloric acid, the tin might be dissolved in ferric chloride, after removal of the excess of zinc, and then determined volumetrically. The metal, being in such a finely divided state, would be very easily soluble in this reagent.

SEPARATION OF COPPER AND CADMIUM.

I find that copper and cadmium may be easily separated by the following method:—

To the neutral solution containing these metals (ammonia salts must not be present) add sodium thiosulphate (hyposulphite) until the solution becomes colourless, then add sodium carbonate, and the cadmium will be precipitated as carbonate (white); filter, and to the filtrate add HCl, and boil, and the copper will be precipitated as sulphide. To use this method in the ordinary course of analysis, the solution, after removal of the bismuth, would

have to be evaporated to dryness and ignited so as to remove all ammonia salts.

ON NEW QUANTITATIVE SEPARATIONS OF
MANGANESE AND NICKEL, MANGANESE
AND COBALT, AND OF MANGANESE,
NICKEL AND COBALT.

By PAUL JANNASCH and CARL J. FRANZKE.

SOME time ago one of the present writers, in concert with Mr. McGregor, succeeded in ascertaining and laying down those conditions under which manganese and zinc may be very conveniently and exactly separated by means of hydrogen peroxide in a strongly ammoniacal solution, and in presence of very much ammonium chloride. We are now in a position to state that the separation of manganese and nickel can be effected under the same conditions and with the same accuracy as that of manganese and zinc.

In view of these experimental facts we hoped to separate manganese and cobalt in the same or in an analogous manner. But our analyses soon showed the impossibility of a quantitative separation of the two metals in the manner adopted, for all our experiments failed by reason of the marked obstinacy with which very considerable quantities of cobalt (on the average several per cents) adhered to the manganese hydroperoxide, so that even precipitations of the manganese several times repeated proved quite unsatisfactory.

After a long series of the most different modifications of the experimental conditions, we found the solution of the double (potassic) cyanide of the metals an excellent means for the quantitative separation of manganese and cobalt. From such a solution hydrogen peroxide throws down manganese absolutely free from cobalt. The behaviour of a solution of potassium-manganese nickel cyanide is quite similar, and, as it might be expected, the corresponding solution of all the three metals concerned. But in the execution of this new process for separating manganese, nickel, and cobalt, certain definite proportions of the reagents to be used are absolutely necessary, as is also the attention to certain precautions, the full description of which will form the subject of a future communication. — *Berichte der Deutsch. Chem. Gesell.*, vol. xxiv., p. 3204.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

November 19th, 1891.

SIR HENRY ROSCOE, F.R.S., in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Hugh Brown Collins, West Balgray, Glasgow; Albert Henry Luckett, Brighton College, Brighton; James Hill Millar, 13, Waterloo Road, Wolverhampton; James Alexander Schofield, University of Sydney, New South Wales; Morris William Trewers, 2, Pnillmore Gardens, Kensington, W.; Hugh Woods, 11, Archway Road, Highgate, N.

The following papers were read:—

67. "Iron Carbonyl." By LUDWIG MOND, F.R.S., and Dr. LANGER.

The authors have isolated two compounds of iron with carbon monoxide, represented by the formulæ $\text{Fe}(\text{CO})_3$ and $\text{Fe}_2(\text{CO})_7$, for which they propose the names ferro-pentacarbonyl and diferroheptacarbonyl.

* From *School of Mines Quarterly*, xii., No. 4.

The ferropentacarbonyl is obtained by exposing finely divided iron in an atmosphere of carbon monoxide at the ordinary temperature during about twenty-four hours, and then heating to about 120° . A small quantity (about 1 grm. from 100 grms. of iron) of an amber-coloured liquid is thus obtained, of the relative density 1.4666, which solidifies below -21° , forming acicular, yellowish crystals. The compound distils unchanged at 102.8° , the vapour having a density of 6.5, that corresponding to the formula $\text{Fe}(\text{CO})_5$ being 6.7. It is not acted on by dilute acids; nitric acid, chlorine, and bromine destroy it; alcoholic solutions of alkalis readily dissolve it, and form red-coloured solutions, which rapidly change in contact with air, but from which, as yet, no definite compounds have been obtained.

Diferroheptacarbonyl is obtained by exposing the liquid ferropentacarbonyl to light. It separates in gold-coloured crystals, carbon monoxide being liberated. The crystals are almost insoluble in all ordinary solvents; they are not volatile, but on heating to 80° they are decomposed into iron, ferropentacarbonyl, and carbon monoxide. The crystals are not changed by dilute acids, but are readily acted on by nitric acid, bromine, and chlorine. Alcoholic potash dissolves them, forming a red solution, very similar to the solution of the ferropentacarbonyl.

A lecture was then delivered on—

"Colour-Photometry." By Captain ABNEY, C.B., D.C.L., F.R.S.

Colour has been usually made the subject of reference to empiric and variable standards, a practice which affords results useless for future reference, and only suitable for present immediate wants. What is required is a reference to numbers which are on some standard scale that can easily be reproduced.

According to the lecturer, the colour of a body, when viewed in a light of standard quality, is known when (a) its luminosity, (b) its hue, and (c) its purity, or the extent to which it is freed from admixture with white light, are known and expressed by numbers.

The luminosity of a colour can be given in absolute number by referring it to the standard of white. Thus, if white light fall on a coloured surface and on a surface of some standard white, the luminosity of the former may be expressed in terms of that of the light. It may appear difficult to compare the brightness of two such surfaces, but as a fact, the comparison is easily accomplished by causing the light falling on the white surface to be rapidly alternately made brighter and darker than that falling on the coloured surface. This can be done by interposing in the beam falling on the white surface rotating sectors with apertures which open and close at will during rotation. The point of equal luminosity can be found by this plan within 1 per cent. Experiments exemplifying the method were made, the brightness of an orange and of a blue pigment being compared with that of a zinc oxide surface which the author uses as standard white. It was also shown by sending the beams through a trough containing water in which mucin was suspended in minute particles, that the relation only held good for the particular light in which it was measured. Hence the necessity for using a standard light.

The luminosity of the light transmitted through coloured translucent bodies was also measured, and the same necessity shown for the use of a standard light.

The standard light recommended was that from the crater of the positive pole of the electric light when high illumination was required, or from a petroleum lamp when the illumination need not be so intense.

The method of measuring the luminosity of light coming through translucent bodies was also shown. A white oblong of paper was placed on a blackened card, a square which occupied half this oblong being pierced in the card, and thus half could be illuminated from the back of the card, and the other half by light from the front by placing a rod in the path of the beam to cast a shadow

on the first half. The translucent substance was placed close behind the aperture in the card, and the light illuminating the paper, after passage through the translucent medium, was measured by altering the illumination of the other half lighted from the front.

The luminosity of the pure spectrum colours may be measured by what the author calls the colour patch apparatus, which is described in the *Phil. Trans.*, 1886, and in his work on "Colour Measurement and Mixture." It essentially consists of a collimator, two prisms, a lens, and a camera, on the screen of which a spectrum is brought to a focus. This screen is removed for experiments, and a collecting lens used to re-combine the spectrum, and to form an image of the last surface of the second prism on a screen some four feet off. A slide with a slit passed through the spectrum causes the white patch to become a colour patch of monochromatic light due to the particular ray traversing the spectrum slit. The white light with which the colour is compared is obtained from the light coming through the collimator and reflected from the first surface of the first prism; by means of a mirror and lens, it forms a patch equal in size to, and which can be caused to overlap, the coloured patch, or to lie alongside of it. In the first case, a rod placed in the path casts two shadows, one of which is illuminated by the colour and the other by the white light; rotating sectors in the path of the latter allow the luminosity to be compared. The light used in the electric light, an image of the crater of the positive pole being formed on the slit of the collimator.

The luminosity of a colour is not the same when viewed from all parts of the eye. The centre of the eye is that with which observations are usually made; hence the luminosity should be measured with that part of the retina, and it is advisable that no more than 6° of angular measure from the eye should be compared.

The audience were enabled to see the difference in luminosity of a colour which was of equal brightness to a certain white when viewed centrally, by shifting the axis of the eye so that the image was received on the retina some 10° away from the centre.

The action of the yellow spot was then alluded to.

The luminosity of any pigment on paper can be found by rotating it with two of the three colours: red, emerald green, and ultramarine.

These three make a grey which matches a grey formed of black and white. If the luminosity of the three have been accurately determined, by substituting the pigment whose luminosity is required for one of them, another grey can be formed to match a grey consisting of black and white. After measuring the angular aperture of the sectors, the luminosity is determined by calculation; the result is found to agree with the measurement made by the direct method. This is one of the many proofs that the measure of luminosity obtained in the manner described is correct, and not a mere accident.

The colour of a pigment can be referred to the spectrum colours by measuring the absorption. In the case of transparent bodies, this is best done by using a double-image prism at the end of the collimator so as to form two spectra on the camera screen. By adjustment, these may be caused to be so exactly one over the other, that the same colour will pass through a slit in them. After emergence from the slit, the rays from the top spectrum are diverted by a right-angle prism, and caught by another which sends them through a lens on to the screen, forming a patch. Another patch as usual is formed by the rays from the bottom spectrum. By placing the transparent body in the path of one of these rays, the absorption can be measured by equalising the brightness of the patches by the sectors and noting the apertures. The absorption of pigments can be measured in the same way by causing one patch to fall on the coloured surface and the other on the standard white.

To measure the absorption of pigments an easy plan is to rotate black and white sectors together with variations

in the amount of white, and to cause the colour patch to fall partly on them and partly on the pigment. The colour is varied till it is seen that the grey disc and the pigment reflect the same amount of light.

By both these plans, templates can be cut out, which, when rotated in the spectrum, give the exact colour of the pigment on the screen; hence this is a reduction of the true colour to absolute numbers, since the colour can be reproduced from a reference to a note book. It is to be remarked that the measures are unaffected by any defect in the eye of the observer, or by the kind of light in which they were effected.

The mixture in varying proportions of red, green, and violet of the spectrum makes white. This was shown by placing three slits in standard positions in the spectrum, and altering their apertures till a match was made with a patch of white light alongside.

Any other colour can be matched by the mixture of the same three colours, as was shown in matching green, blue, and brown papers.

Since three colours will make white, and the same three colours will make a match with an impure colour, every colour in nature can evidently be matched by mixing not more than two of these colours with a certain proportion of white light; and if these colours be red and green, or green and violet, the colour can be matched by one spectrum colour and white light, since there is some intermediate colour which has the same hue as the mixture of these two colours. Hence any colour, except purple, can be referred to some spectrum colour, together with a certain proportion of white light. In the case of purple, the colour may be expressed as white light, from which the complementary colour is eliminated. Hence any colour whatever may be expressed in terms of white light and one spectrum colour, the latter in wave-lengths, and the former in percentage of luminosity.

This was shown to be the case by interposing between the silvered mirror which reflected the light coming from the first prism, and which formed the white comparison patch, a plain glass mirror which reflected a small percentage of the light on to the colour patch, the amount of which could be regulated by sectors. Brown paper was placed in the white patch, and the spectrum colour was changed and mixed with the white light till the same colour was obtained. The scale of the instrument told the wave-length, and, by interposing a rod in the path of beams, the proportional luminosities of the spectrum colour and of the white light were determined. A similar match was made by light going through signal-green glass, and the complementary colour of the light passing through permanganate was determined.

Light coming through properly picked specimens of red, blue, and green glass, and overlapping, may also be made to match a colour.

The three glasses covered a square lens, and formed an image on a screen of a circular patch of white light coming through ground glass on a screen. Colours were placed on a white beam alongside, and by altering the amount of the coloured glasses exposed, matches were made.

If the dominant wave-lengths of the colour of these three glasses be known, and also the amount of white light mixed with it, these measures can be noted in terms of these three glasses; and, further, it is possible, by mixing the light coming through the three glasses in various proportions, to obtain a spectrum colour mixed with white light for each such mixture. Hence this is a substitute for the spectrum itself. To show this, three similar glasses were placed over apertures suitably cut in a circular card; and, by causing these to rotate in front of an illuminated slit, a sham spectrum was thrown on the screen in which every colour was present.

Any colour can be reproduced with three rotating sectors of red, green, and blue, when certain proportions of white or black, or both, are mixed with one or other. If the dominant wave-lengths and the proportion of white light

mixed are known of each such colour, the pigment whose colour is to be determined can be expressed in numbers as before, and in terms of spectrum colours if desired. This was shown by matching brown paper with red, blue, and green, a little white and black being mixed with the brown.

The importance of using some uniform light was insisted upon throughout, slight deviations in the experiments demonstrating this.

In conclusion, Captain ABNEY claimed to have demonstrated that the reference of colour to numbers was not only possible but easy, and that, to chemists especially, the application was one of almost capital importance. Everyone could do it, and the lecturer had an instrument on the stocks which was not so cumbersome as that shown, but which would answer all purposes, he hoped, when complete.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, December 7, 1891.

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Institution:—Lorentz Albert Groth; John Imray, M.A., M.Inst.C.E.; George Stillingfleet Johnson, F.C.S.; John List, M.Inst.C.E.; Mrs. Douglas Powell; James Shand, M.Inst.C.E.; Mrs. Thomas Threlfall.

The Special Thanks of the Members were returned for donations from Professor Dewar (for structural alterations); from Mr. Ludwig Mond (for new pressure pump).

The Chairman reported that the late Mr. J. P. Stocker had bequeathed £100 to the Royal Institution.

The Presents received since the last meeting were laid on the table and the thanks of the Members returned for the same.

CORRESPONDENCE.

THE DETERMINATION OF THALLIUM.

To the Editor of the Chemical News.

SIR,—In the number of your journal issued November 13th there is an article by M. Baubigny on the "Determination of Thallium," from which it appears that the author has completely overlooked my experiments on that subject, published in the *Journ. Anal. Chem.*, 1888, page 243. (See also *Zeit. fur Anal. Chem.*, 1891, 342.) In my investigations I determined the solubility of thallous iodide under various conditions, and reached conclusions not essentially different from those of M. Baubigny. The collection and weighing of the precipitate on a Gooch filter, which I recommend, is certainly far more accurate and convenient than is the method followed by this chemist.

I will add here that the Gooch filter, whose merits do not seem to be fully understood and appreciated abroad, is described in the *CHEMICAL NEWS* of May 3rd, 1878.—I am, &c.,

JOHN H. LONG.

Chicago, Nov. 24, 1891.

The Use of the Pendulum as a Balance.—K. Fuchs (*Zeit. Phys. Chemie*).—The centre of gravity of a pendulum rod about 2 d.m. in length, lies rather above the fulcrum. Check-pieces on both sides of the top prevent the rod from turning over when not loaded. The lower end carries a basket to receive the body to be weighed, and so many weights that the centre of gravity falls somewhat below the knife-edge support, whereby the rod is able to make slow oscillations of 5–10 seconds duration. The weight of the body can be calculated from the time observed according to a method given.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

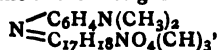
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlii., No. 21, November 23, 1891.

Preparation and Properties of the Boron Phosphides.—Henri Moissan.—The author, taking boron phosphide as his point of departure, has obtained two boron phosphides. One of these, PB, combines with incandescence with monohydrated nitric acid, and takes fire in the cold if immersed in chlorine. The other compound, P₃B₅, is much more stable, and is not decomposed in the cold by these two reagents.

Mechanical Determination of the Position of the Atoms of Hydrogen in Organic Compounds.—G. Hinrichs.—The author concludes that the primitive form, CH₄, of organic compounds cannot be a tetrahedron, of which the atoms of hydrogen form the corners whilst the atom of carbon is the centre. On the contrary, the four atoms of hydrogen of CH₄ form the angles of a square above the square surface of the atom of carbon.

On Aniline Black in Dyeing by the Dry Way.—S. Grawitz.—The writer proposes to add to Lightfoot's formula for aniline blacks alkaline or earthy alkaline bases in the state of organic salts, such as acetates with or without an excess of organic acid. This black is said not to smear off.

On a Codeine Violet.—P. Cazeneuve.—This compound, to which the author assigns the formula—



dyes wool, silk, and gun-cotton, like morphine violet. Light slightly affects the colour. The yield of the product is small.

The Distribution of Saccharine Matters in the Different Parts of Boletus Edulis.—Em. Bourquelet.—Trehalose is chiefly found at the foot of the fungus. Glucose exists in a much smaller proportion. Neither of these sugars is present in the hymenophore.

Moniteur Scientifique, Queneville.
Series 4, Vol. iv., Part 2, No. 588.

Schmidt's Process for Converting Oleic Acid into Solid Fatty Acids (*Monatshfte fur Chemie*).—The methods of conversion founded on the action of nitrous acid, of chlorine, bromine, and iodine, or of melting potassa, are not economical, and sometimes too delicate for industrial use. Schmidt heats 10 parts of oleic acid to 180° with 1 part of zinc chloride. The reaction is complete when a drop of liquid taken from the melted mass and boiled in a test-tube with diluted hydrochloric acid solidifies on cooling. The whole is then dissolved in the same dilute acid, boiled by passing a jet of steam into the liquid, the aqueous portion is removed by decantation, and this operation is repeated as long as the acid extract still contains zinc. The product is then washed with water and distilled in superheated steam with an ordinary rectifier. The operation is completed by removing any unconverted oleic acid by pressure or by centrifugal action.

Specific Weights of Certain Fats and Oils.—C. A. Crampton.—(From the *Amer. Chem. Jour.*).

Characters of Castor-Oil.—H. Gilbert (*Chem. Zeit.*).—Castor-oil should have a specific gravity of 0.950–0.970; it becomes turbid at 0°, with a separation of crystalline flakes; at lower temperatures it takes the consistency of butter, and mixes in all proportions with alcohol and acetic acid. A mixture of 3 parts castor-oil, 3 parts carbon bisulphide, and 2 parts sulphuric acid

should not take a brown colour. A castor-oil which becomes turbid with petroleum benzene, and gives a clear solution with 5 vols. of alcohol at 90°, may be considered as pure. These characters serve to detect the presence of extraneous fatty oils in castor-oil, but not that of resin oil. The latter has a specific gravity of 0.96–0.99, and is soluble in alcohol and acetic acid. On saponifying the oil with soda-lye, shaking the aqueous solution with ether, and expelling the latter by distillation, there remains, if resin oil be present, a residue having all the properties of resin-oil. Pure castor-oil, if shaken up with an equal weight of nitric acid at 1.31, turned slightly brown, whilst the acid remained colourless. Resin oil, if treated in the same manner, becomes almost black, whilst the acid turns of a brownish yellow.

Action of Chlorine upon Hæmatoxyline, and on the Extractive Matter of Logwood.—W. McFarlane and P. S. Clarkson.—(From the *Jour. Frank. Inst.*).

Manufacture of Colourless Tannin.—A. Villon.—(From the *Bulletin de la Soc. Chimique*).

Chemical Section of the Industrial Society of Mulhouse.—A "sealed paper" deposited in 1880 by Zurchers, of Cernay, asserts that the authors have obtained aniline black by treating a salt of aniline at a gentle heat with a solution of ammoniacal copper sulphate. Henri Schmidt sent in a paper accompanied with swatches, illustrating a new process of discharging chrome-colours before their development by steaming. A colour of chrome, galloxyaniline, alizarin blue, &c., is padded upon the cloth. There is then printed on a discharge consisting of red prussiate, an alkaline chlorate, and magnesium carbonate, and the pieces are steamed, producing a white design. To this discharge is added any albumen colour to produce coloured discharges. M. Prud'homme has noticed that the solubility of tartar emetic in common salt is due to the fact that these two salts form a molecular combination, containing 1 mol. tartar emetic to 4 mols. sodium chloride. This combination renders it possible to produce a colour which is at once very concentrated and soluble, and which may be prevented from running by adding a larger proportion of tannin. M. Jacquet has observed that soap-baths soiled by aniline colours may be restored by adding a certain quantity of antimony tannate, which precipitates the aniline colour as an insoluble lake.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements before Easter:—Professor John G. McKendrick, six Christmas Lectures to Juveniles, on Life in Motion, or the Animal Machine; Professor Victor Horsley, twelve lectures on The Structure and Functions of the Nervous System (the Brain); Mr. A. S. Murray, three lectures on Some Aspects of Greek Sculpture in Relief; Professor E. Ray Lankester, three lectures on Some Recent Biological Discoveries; Professor W. P. Ker, three lectures on The Progress of Romance in the Middle Ages; Dr. B. Arthur Whitelegge, three lectures on Epidemic Waves; Professor J. A. Fleming, three lectures on The Induction Coil and Transformer; The Right Hon. Lord Rayleigh, six lectures on Matter—at Rest and in Motion; Professor J. F. Bridge, three lectures on Dramatic Music, from Shakspeare to Dryden (the Play, the Masque, and the Opera), with illustrations. The Friday Evening Meetings will begin on January 22nd, when a Discourse will be given by the Right Hon. Lord Rayleigh on The Composition of Water; succeeding Discourses will probably be given by Sir George Douglas, Bart.; Professor Roberts-Austen, C.B.; Mr. G. J. Symons; Professor Percy F. Frankland; Sir David Salomons, Bart.; Professor L. C. Miall; Professor Oliver Lodge, Mr. George du Maurier; Mr. John Evans; Mr. F. T. Piggott; Professor W. E. Ayrton, and other gentlemen.

MEETINGS FOR THE WEEK.

- MONDAY, 14th.—Society of Arts, 8. "The Pigments and Vehicles of the Old Masters," by A. P. Laurie, M.A.
Medical, 8.30.
- TUESDAY, 15th.—Institute of Civil Engineers, 8.
Pathological, 8.30.
- WEDNESDAY, 16th.—Society of Arts, 8. "Typological Museums, as Exemplified by the Pitt Rivers Museum at Oxford," by General Pitt Rivers.
Meteorological, 7.
Microscopical, 8.
- THURSDAY, 17th.—Royal, 4.30.
Chemical, 8. "The Composition of Cooked Vegetables," by Miss K. Williams. "On some Metallic Hydrosulphides," by S. E. Linder and H. Picton. "On the Physical Constitution of some Solutions of Insoluble Sulphides," by H. Picton. "Solution and Pseudo-Solution," by H. Picton and S. E. Linder. "The Change Proceeding in Acidified Solutions of Sodium Thiosulphate when the Products are Retained Within the System," and "The Action of Sulphurous Acid on Flowers of Sulphur," by Dr. A. Colefax. "The α and β Modifications of Chlorobenzene Hexachloride," by Dr. Matthews. "Camphrene, a Product of the Action of Dehydrating Agents on Camphor," by Drs. Armstrong and Kipping. "Studies on the Dibromonaphthalenes," by Dr. Armstrong and Mr. Roosier.
- FRIDAY, 18th.—Physical. "On Interference with Alternating Currents," by Mr. H. Kilgour.
Quekett Club, 8.

TO CORRESPONDENTS.

Saponification of Beef Fat.—We have received several letters on this and the allied subject of the Saponification of Butter. As, however, the discussion is losing its scientific character and becoming too personal to be of general interest, as no new facts of importance seem to be forthcoming, and as the correspondence cannot go on for an indefinite time, we shall ask our correspondents' pardon for closing the discussion.—Ed. C. N.

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THE VALUATION OF COAL FOR USE IN STEAM BOILERS.

By THOMAS T. P. BRUCE WARREN.

THE evaporative power of a substance, when burnt under the most favourable circumstances, affords a tolerably accurate method of estimating its intrinsic value as a fuel. Evaporative power is taken as being the quantity of water lost by evaporation at 212° F. in a given time per unit weight of fuel, say, one pound, the initial temperature of the water being 60° F.; the barometric column being normal.

In carrying out the principle for the actual generation of steam in a steam boiler so as to obtain comparative results for different kinds of coal, we have a variety of conditions to contend with. The same coal may be burnt in a furnace constructed as perfectly as possible with respect to area of grate, draught of air, flues, and chimney, and still yield results which vary from those obtained with the same coal burnt under another boiler, the setting, &c., of which is practically the same as in the other case.

Priming and the escape of aqueous vapour with the steam, introduce elements of uncertainty. Hence, it is usual to take the average consumption of coal corresponding to an ordinary day's work; assuming, of course, that the consumption of steam is as near as possible uniform, and the personal equation of the fireman, as far as this function is admissible, beyond reproach. The state of the boiler, as regards fur or scale, sooty deposit, &c., even if the supply of water be accurately measured, will materially affect the result.

Mechanical stokers and mechanical shifting fire-bars will eliminate the variations introduced by hand firing and the occasional opening of the furnace doors to clean the bars. So far, the average value of different kinds of coal for generating steam at a given pressure may be taken as practically near enough.

If we estimate the chlorine per gallon in a boiler when filled to its working level, and again after two or three hours' run, the water evaporated can easily be ascertained, irrespective of spasmodic demand or lull in steam supply. By estimating the chlorine from time to time, we get a far better idea of what a boiler is doing.

We have first to ascertain the chlorine, in grms. per gallon, in the feed water, and dividing the quantity of chlorine found in the boiler water, after a few hours' run, we get a ratio for the number of gallons evaporated; multiplying the number of gallons contained in the boiler at its working level by this ratio, we get the number of gallons evaporated or concentrated to the original water level.

As the chlorides in water are all soluble, and by keeping the water slightly alkaline, so as to avoid loss of chlorine, we have an accurate and trustworthy method of finding out what a given weight of fuel has driven off in steam. Loss of chlorine and priming are the only elements likely to disturb the reliability of the result. The blow-off cock should not be used whilst these experiments are in hand. Water thickened by evaporation should be avoided by filling the boiler with fresh water on starting.

Apart from the valuation of fuel, the information thus obtained will give a very accurate idea of the state of different boilers as regards scale or fur, setting, draught, &c.

Let C be the chlorine in grains per gallon of the feed water, and let C' be the chlorine found after a certain

number of hours' run; let G be the number of gallons in the boiler to the working level, then—

$$\left(\frac{C'}{C} \times G\right) - G =$$

number of gallons evaporated.

The ratio $\frac{C'}{C}$ should be nearly constant for the same

construction and capacity of boiler when worked for the same number of hours and generating the same quantity of steam, but if the steam be generated faster, we may conclude that the conditions for evaporation are more favourable and *vice versa*. If the boilers are equally free from scale, and the generation of steam unequal, it will generally be found that the draught is better in one case than in another, or the escape of steam is unequal.

It is not uncommon to find in a set of boilers working together that $\frac{C'}{C}$ is by no means uniform for each boiler;

hence the practice of blowing off or emptying after a stated period of working may be wasteful or dangerous. It is far better to be guided by a reliable hydrometer, and to blow off when the water attains a certain density. If the feed water be evaporated to any given fraction of its original bulk, and the corresponding density taken, we can determine the degree of concentration corresponding to the diminished bulk, and as this can be carried out by anyone not accustomed to chlorine determinations, there is no reason why any steam-user should not have some tolerably accurate idea of the concentration taking place in a steam boiler.

Taking density instead of chlorine, we may write $\left(\frac{D' - 1}{D - 1} \times G\right) - G =$ number of gallons evaporated.

In this case, D is found by experiment, by first boiling the water, so as to throw out of solution what would be thrown out in the boiler, then making up with distilled water the loss on evaporation. In this formula the specific gravity of pure water = 1.

Let D be the initial density, and D' the density at the end of time, T; then D' - D is the increment of density corresponding to T, and $\{(D' - D)n\} + D$ will be the density at end of n times T.

The experimental verification may be simplified by taking a given volume of water, say five gallons, and evaporating to one pint or less, making up to one pint with distilled water; when cooled to 60° F. the specific gravity is taken, which corresponds to a concentration of 40 to 1. We then mix the above pint with one pint of feed water; the specific gravity of the mixture corresponds to a concentration of 20 to 1; by mixing this again with an equal volume of feed water we have a concentration of 10 to 1. The dilutions may be varied so as to give as many degrees of concentration as we please.

In this way we can see at once what our fuel is doing, and can check the results as often as we please without any interruption to the usual methods of valuation.

I may remark that the water from a boiler containing saline scale would vitiate the result in either case; thus, the salt dissolved out with boiling would give too high a result in the chlorine estimation, and also in density. The information thus gained would be very useful, as a steam-user would know that he had accumulated salt in his scale, and would blow off more frequently, so as to get rid of it.

On Nitrosulphobenzoic Acid and its Salts, $C_6H_3(COOH)(\text{SO}_3H)NO_2(1.2.4)$.—M. Hauser.—The author has previously mentioned the curious fact that the nitrosulphonic acids of benzene and toluene displace sulphuric acid from some of its salts. The nitrosulphobenzoic acid possesses this property in a more striking degree. The author has obtained and examined the dipotassium, monopotassium, and lead salts of the acid.—*Bull. Soc. Chim. Paris*, vi., No. 6.

NITROHYDRIC ACID.*

By TH. CURTIUS.

THE investigations on azoimidic acid have been delayed by a serious accident which occurred to one of his pupils whilst preparing the anhydrous acid. The immediate object is to find methods of obtaining this remarkable substance and its compounds without danger,—at least, those compounds the manipulation of which is not perilous. Such are above all the ammonium salt and the diammonium salts of nitrohydric acid, N_4H_4 , N_4H_5 , and N_4H_6 ; further, the salts of nitrohydric acid with the metals of the alkalis and the alkaline earths.

The methods had to be selected so that the preparation of the free acid was dispensed with under all circumstances. This end was reached in the following manner.

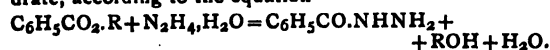
Formation of Nitrogen-Alkaline Metals.

1. From the nitroso-hydrazines, or from the azoimides by the spontaneous splitting off of water by the action of alkalis in an alcoholic solution.

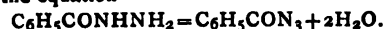
2. From a quite new class of organic compounds which contain three atoms of nitrogen as an open, non-ramified chain, and which are to be regarded as derivatives of hydronitrogen, NH_2-N-NH , analogous to the hydrocarbon propylene, $CH_3-CH=CH_2$.

Preparation of Sodium-Nitrogen from Benzoylazoimide.

According to the researches of Curtius and Struve, benzoic ether is converted almost quantitatively into benzoylhydrazine, $C_6H_5CONHNH_2$, by hydrazine-hydrate, according to the equation—



From benzoylhydrazine there is formed, as the author has previously stated, benzoylazoimide, $C_6H_5CON_3$, by the action of sodium nitrite and glacial acetic acid according to the equation—



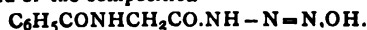
Benzoylazoimide is dissolved in an equal weight of absolute alcohol, to which is added an atom of sodium dissolved in a little absolute alcohol, and the mixture is digested for some hours on the water-bath. There are formed benzoic ether and nitrogen.—sodium according to the equation—



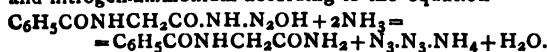
On the addition of ether the sodium compound falls down almost in a theoretical proportion after a portion has already crystallised out the alcoholic solution on cooling. The filtrate is distilled, and thus almost the calculated quantity of benzoic ether is recovered, and may be converted into the initial material benzoylhydrazine. The nitrogen-sodium thus obtained is pure.

Preparation of Nitrogen Ammonium from the so-called Nitrosohippurylhydrazine.

Quite as convenient is the preparation of the nitrohydric salts from the product of the reaction of nitrous acid upon hippurylhydrazine. The substance was first regarded as nitroso-hippurylhydrazine, but it is a diazo-compound of the composition—



This substance cannot be converted into hippurylazoimide with a splitting off of water; but if dissolved in alcohol, and the liquid is saturated with gaseous ammonia, it is resolved quantitatively into hippuramide and nitrogen-ammonium according to the equation—



This diazohippuramide is obtained from hippuric ester in calculated quantity. A pound of the substance is

covered in a two litre flask with 600 grms. of alcohol at 85 per cent, and whilst the flask is refrigerated ammoniacal gas is introduced to saturation. It is then allowed to stand for 24 hours, and the liquid is boiled with a reflux condenser until ammonia ceases to escape. After cooling for 12 hours the mass of crystals which has separated is drained and washed with cold alcohol. From the alcoholic filtrate 4 vols. ether precipitate about 70 per cent of the nitrogen ammonium in a pure state as a white powder. The rest of the compound can easily be recovered by re-crystallising the hippuramide from water, and mixing the mother-liquor with the ethereal alcoholic filtrates. It may thus be obtained as a lead, a silver, or a mercurous salt. The treatment of these compounds is very dangerous. The precipitated nitrogen-ammonium is washed with ether and dried in the air. The pure hippuramide is re-converted into hippurylhydrazine with escape of ammonia by boiling with hydrazine-hydrate.

Diazohippuramide

The author will subsequently, in concert with H. Lang, describe this remarkable body in full. For the present I merely say that diazohippuramide is one of the substances most capable of reactions which I have ever encountered. It combines with the representatives of nearly all classes of bodies, organic and inorganic, partly in the cold and in two very different manners:—(1) either nitrohydrogen is split off (action of alkalis, ammonia, aniline, toluylendiamine, diamide, phenylhydrazine; (2) or there escapes nitrogen (action of water, alcohol, halogenous alkyls, aldehyds, halogens, acidyl hydrazines).

(To be continued.)

THE BEHAVIOUR OF AZOIMIDE WITH LIVING ORGANISMS.*

By O. LOEW.

(Concluded from p. 288).

AN experiment executed on a rabbit by Dr. Pfeiffer, of the Hygienic Institute of Munich, in conjunction with the writer, gave the following results:—Eight minutes after the subcutaneous injection of 0.03 grm. sodium azoimide, there occurred muscular tremblings; ten minutes later increased secretion of saliva, lameness of the anterior extremities and retardation of the movements of the heart. After sixteen minutes, cramps, phenomena of lameness in the hinder extremities, inability to rise up again after falling. Soon afterwards, great difficulty of breathing, interrupted by single cramps, which continued until death—1 hour 44 minutes after the injection.

It may here be mentioned that I, after intentionally inhaling an atomised 1 per cent solution of sodium azoimide, soon experienced a ringing in the ears and headache, which lasted for about twenty-five minutes. Th. Curtius mentioned that free azoimide if respired occasions dizziness, headache, and inflammation of the nasal mucous membrane, and that the aqueous solution has a corrosive action upon the epidermis.

If we inquire the cause of the intense toxic action of azoimide, the most plausible view is the following:—Azoimide and its compounds are, as Curtius observed, easily decomposed and with a violent explosion. As the vital activity of the cells sets up decomposition by the transfer of violent atomic vibrations, the sudden decomposition of the azoimide compounds may react upon the protoplasm and occasion a re-arrangement of the active proteine matter.

In general, those cells and organisms will perish most rapidly by the action of azoimide, which decomposes it

* Berichte der Deutsch. Chem. Gesell.

* Ber. der Deutsch. Chem. Gesell.

most quickly. If the cells are ganglionic cells, such phenomena may act as irritations, and being conducted away in the nerves, they may appear as cramps in the muscles. The destructive process, introduced by rapidly succeeding irritations, can be propagated in the nerves like fire in a match, and bring the entire system into decomposition, when the death of the muscular and glandular system follows secondarily in consequence of the inaction of the heart and lungs.

In azoimide we have certainly another cause of toxic action from hydroxylamine and diamide. If the compound, supposed by Curtius, $\text{NH}_2\text{—NH—NH}_2$, can be really isolated, we shall find it a most intense poison. In hydroxylamine and diamine we recognise a specific chemical action—an attack upon the aldehyd groups which occurs even if highly diluted. Azoimide will exert an action upon the aldehyds—if at all—only when in a very concentrated solution.

The slow action of sodium azoimide upon *Algæ* is very striking. We observe here that with a solution of 1 per 1000, granulations appear only after the lapse of several days, a fact which certainly indicates a slow decomposition, for if the sodium azoimide as such were capable of producing granulations, these would become visible in all spirogyrenous cells—at the furthest after some hours. Ammonia is probably formed, for whether in the free state or as carbonate, even at 0·1 per thousand, it produces the same phenomena of granulation. Ammonium salts of a neutral reaction act in the same manner at a concentration of 1 per 1000, but not at 0·1 per thousand. At the latter dilution ammonia exerts merely a nutritive influence.

Azoimide may apparently yield most readily ammonia by fission with water, nitrous oxide being formed simultaneously, $\text{N}_3\text{H} + \text{H}_2\text{O} = \text{N}_2\text{O} + \text{NH}_3$.

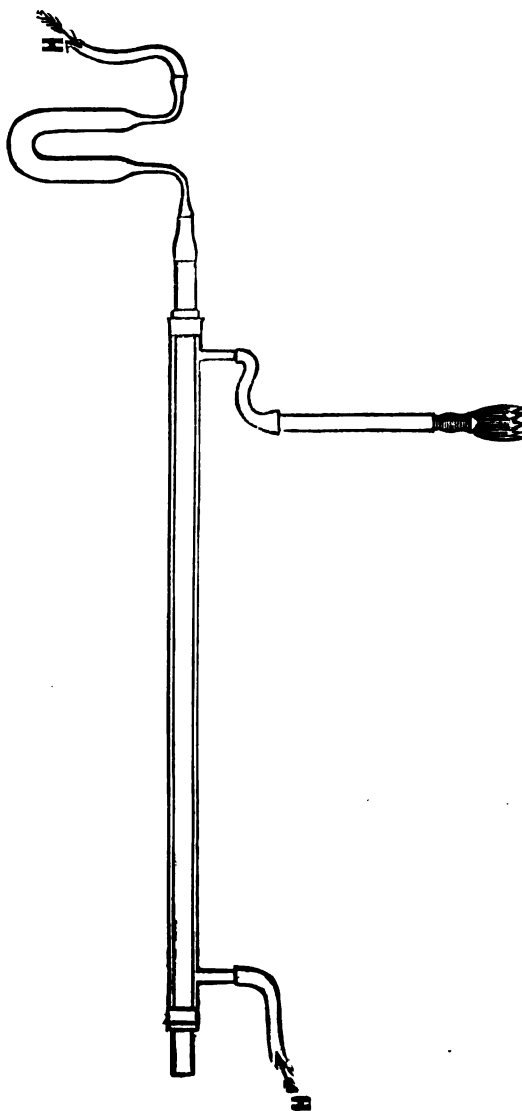
As the chemical activity of protoplasm reminds us of catalytic actions, I tried if platinum black could produce a similar fission, and heated the small residue of 1 per cent solution of sodium azoimide, which I had at my disposal, with about 10 grms. of powerfully active platinum black. Immediately there occurred a violent disengagement of an indifferent gas, and the liquid, which had become highly alkaline, gave an extremely strong ammoniacal reaction with Nessler's reagent. On the addition of dilute sulphuric acid the reaction became still more energetic. Azoimide, therefore, can in fact yield ammonia by catalytic decomposition, and thereby my view as to its action upon *Algæ* acquires more probability. As already mentioned, I consider its far more rapid action upon other organisms of a vegetable or animal origin from a different point of view.

DISSOCIATION OF PHOSPHONIUM BROMIDE.

By G. S. NEWTH.

It is a well-known fact that phosphonium chloride is completely dissociated at ordinary temperatures into phosphoretted hydrogen and hydrochloric acid, and that the compound can only exist under the influence of either cold or pressure. The corresponding compound with hydrobromic acid, however, is much more stable, and if the two gases, phosphoretted hydrogen and hydrobromic acid, be mixed together, white fumes are at once produced, which condense at the ordinary temperature to a solid mass resembling ammonium chloride in appearance. The compound, however, undergoes partial dissociation even at the ordinary temperature, which may be shown by the following simple device, which forms a very convenient and striking lecture experiment for illustrating the phenomenon of dissociation. A glass tube 30 c.m. long and 10 m.m. bore, has blown upon it two small branch tubes at a short distance from the ends; the stem of a long clay tobacco pipe is passed through the glass tube,

projecting about 2 c.m. beyond each end, and secured in its place by small pieces of caoutchouc tube being inserted between the glass and the clay pipe,—the whole resembling an ordinary Liebig's condenser in miniature, with a pipe-stem for the inner tube. As it is not often that a pipe-stem of the length required is found sufficiently straight to allow of its passing down a glass tube of the size mentioned, two short pieces may be joined together by a piece of caoutchouc tube. A slow stream of hydrogen is then passed through the glass tube, and burnt at a fish-



tail burner which is screwed into a short piece of lead pipe, and connected to one of the branch tubes of the apparatus, which may be conveniently supported in a horizontal position. A small U-tube, containing a few crystals of phosphonium bromide, is connected to one end of the clay pipe and a slow stream of hydrogen gas passed through. Almost immediately the flame of burning hydrogen will become coloured with the characteristic appearance due to the presence of phosphorus, the comparatively light phosphoretted hydrogen having diffused through the porous clay pipe into the stream of

hydrogen circulating through the glass tube. A piece of blue litmus paper exposed to the gas which issues from the open end of the clay pipe will be at once reddened. If the U-tube be slightly warmed by merely grasping it in the hand, the effect will be still more marked.

The phosphonium bromide is readily obtained by delivering into a flask, immersed in a freezing mixture, a stream of phosphoretted hydrogen and of hydrobromic acid through separate tubes; the two gases combine and the salt deposits upon the sides of the flask. The phosphoretted hydrogen may be prepared by the action of phosphorus upon alcoholic potash, and should be collected in a gas holder. The hydrobromic acid is most conveniently obtained by the method described in the *CHEM. NEWS* of October 30, as by that plan of preparing it the stream of gas can be regulated practically to any desired rate.

The phosphonium bromide obtained in the flask is for greater convenience transferred to a number of small U-tubes, the ends of which are drawn out. This is effected by removing the flask from the freezing mixture, and fitting into it a cork carrying two tubes, one of which passes nearly to the bottom of the flask. A stream of hydrogen is passed through the flask, which may be very gently warmed, and the issuing gas led through one of the U-tubes, which is placed in the freezing mixture. In a few minutes sufficient of the compound will have condensed in the tube, which may then be sealed off. In this way a number of tubes may be quickly filled.

NOTE ON AN ELECTROLYTIC METHOD OF PREPARING METALLIC ALLOYS, &c.

By H. N. WARREN, Research Analyst.

THE following method of preparing metallic alloys, such as silicides, chromides, bronzes, &c., has lately been satisfactorily followed. It differs slightly from the manner in which mercury amalgamates, or alloys, with other elements, owing to its liquidity. By substituting for the mercury, iron, copper, zinc, &c., these metals may be readily made to combine with the more oxidisable elements, such as silicon, boron, phosphorus, &c., by so arranging the process that the metal forming the alloy, when in a fluid state, is connected to the negative pole of a voltaic series, and in direct contact with the substance containing the element with which it is desired to combine it. The apparatus employed consists of a deep conical crucible, through the bottom of which is inserted a pointed graphite rod, projecting about an inch within, the remaining portion being protected by passing through an iron tube coated with borax in order to prevent oxidation when exposing the same to an elevated temperature. The further extremity is next furnished with a binding screw or clamp, and connected negatively with the batteries employed, the whole arrangement being raised to a temperature sufficient to render liquid the metal introduced to form the alloy. Taking, for instance, the preparation of silicides, having introduced into the crucible a sufficiency of metallic copper, add sufficient potassium silico-fluoride to form when melted a layer about two inches in depth; a thick platinum wire is now arranged so that its point just touches the surface of the melted silico-fluoride (care being taken that the melted copper remains sufficiently low so as not to come in contact with the positive pole or platinum wire, otherwise the action is, of course, neutralised and the power of the batteries uselessly exhausted).

To this wire is connected the positive pole of not less than two large cells of the ferric chloride battery, when an instantaneous action is at once perceptible; dense white clouds of hydrofluoric acid are at once evolved from the platinum wire; the potassium silico-fluoride

becomes in part decomposed, the whole of the silicon thus set free uniting with the metallic copper, to form a brittle silicide. Phosphor and other bronzes may, by slight alteration, be also readily formed.

The earthy metals, barium, strontium, and calcium, have as yet not been satisfactorily obtained as alloys.

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ON META-TITANIC ACID AND THE ESTIMATION OF TITANIUM BY HYDROGEN PEROXIDE.*

By Prof. F. P. DUNNINGTON.

THE detection and estimation of small amounts of titanic acid, which has long been very tedious and unsatisfactory, has been rendered exceedingly simple through the publication of A. Weller in the *Ber. der Chem. Ges.*, 1882, of a method depending upon the production of a compound of intense yellow colour by the addition of hydrogen peroxide to the solution of titanium.

Since its publication I have made considerable use of this method, but have recently noted a feature in the test which must be kept in view to avoid error. The solution of the melt obtained by fusion with acid sodium sulphate when made with dilute sulphuric acid of five or more per cent, gives constant results, which tally with those made gravimetrically; but when water only or very dilute acid is employed, one may obtain lower results. Upon one occasion a colouration was obtained which corresponded to only about one-third of the titanium which was afterwards found to be present. Moreover, if we take a slightly acid solution of titanium sulphate, dilute it and heat until it is partially precipitated, cool, re-dissolve with sulphuric acid and then add hydrogen peroxide, the yellow colouration will correspond to only a portion of the titanium present. I find an explanation of these facts in the formation of some meta-titanic acid. It is uniformly stated that when titanic acid is precipitated by heating a not too acid solution, it separates in the form of meta-titanic acid.

In order to further examine the meta-titanic acid which was in part described by Weber (*Jahr.*, 1863, p. 210), I have isolated it as follows:—Heat a dilute solution of titanium sulphate to 100° C.; gradually add ammonia to excess, filter, treat the washed precipitate with hydrochloric acid, and warm; there results a residue which is nearly insoluble in strong hydrochloric acid. Now wash this once or twice by decantation with cold water, and, when most of the hydrochloric acid is removed, there will be left a mass perfectly and readily soluble in cold water.

Again, if the above precipitate is treated with hydrochloric acid, and then evaporated upon the water-bath to remove the latter acid, there is left a mass of scales of a gummy appearance, which dissolves in a moderate amount of water, giving an opaline solution. This substance is practically free from chlorine and contains one molecule of water to one of titanic acid—and so presents the composition of the air dried meta-titanic acid of Merz. If either of these water solutions of meta-titanic acid be treated with hydrogen peroxide, it will not be coloured yellow, but afford a white precipitate.

It therefore appears probable that after the fusion of titanic oxide with acid sodium sulphate, if the melt is digested in water only, the solution of the free acid may occasion sufficient heat to form some meta-titanic acid, which when re-dissolved by the further admixture of acid would not be coloured by the hydrogen dioxide.

And we conclude that in making the estimation of titanium by the method of A. Weller, the "melt," after cooling, is to be digested in dilute sulphuric acid of such

* *Journal of the American Chemical Society*, Vol. xiii, No 7.

11. 1.5700 grm. (dry) gave a loss of 0.0316 grm. after six hours heating in hydrogen. 1.1179 grm. of the reduced mineral gave 1.05 per cent of nitrogen, and 0.4177 grm. gave 81.46 per cent of UO_2 , both calculated to unreduced mineral. The loss in weight should represent 0.0067 water, 0.0206 oxygen from UO_3 , an uncertain amount from Fe_2O_3 , and possibly from PtO , and the difference between 2.41 and 1.05 per cent nitrogen. But it does not exceed the sum of water and oxygen alone, and as in the first experiment no nitrogen seems to have been removed, although quantitative tests show that much has disappeared. Further tests at a higher temperature in a crucible, whereby some lead was reduced and partly volatilised, showed that all the nitrogen could be caused to disappear.

These results are as perplexing as those obtained by heating in air, and the explanation when found will doubtless lead to one for the other case. The apparent failure to expel nitrogen by hydrogen might be taken as additional evidence of its combination with uranous uranium, but it is as difficult to conceive why it should not still be set free by sulphuric acid after reduction of the UO_3 , as after oxidation of a portion of the UO_2 to UO_3 .

Conclusions.

Briefly summarised, the conclusions are as follows:—

1. Nitrogen exists in uraninite in quantities up to over 2.5 per cent, and seems generally to bear a relation to the amount of UO_2 present. This is the first discovery of nitrogen in the primitive crust of the earth, for the nitride of iron found by Silvestri (*Gaz. Chim. Ital.*, 1875, vol. v., p. 303) in lavas from Etna is of recent and secondary origin. It is rather strange that no works on mineralogy, so far as I am aware, make mention of his species.

2. The condition in which the nitrogen exists is unknown, but it is entirely different from any hitherto observed in the mineral kingdom, being liberated as nitrogen gas by non-oxidising acids and by fusion with an alkaline carbonate. Fusion with caustic alkalies does not give rise to the formation of ammonia, but probably liberates nitrogen.

3. Analysis of uraninite from various localities has shown that, with in general the same constituents, the mineral varies widely in composition, and that its physical characteristics and its behaviour toward certain solvents are often as distinct as the chemical differences.

4. The formulæ of Comstock and Blomstrand are in applicable to the zirconia, thoria, and yttria uraninites of North America and Norway, among which are to be reckoned bröggerite, cleveite, and nivenite, and probably to the varieties free from earths.

5. Extended and most careful examination of uraninite specimens from all possible localities is necessary before any conclusion worthy of acceptance can be reached as to the character of the chemical combination, or combinations, represented by them. The work in this direction should likewise cover a study of the nitrides and oxynitrides of uranium and thorium, with synthetical experiments aiming at the artificial production of uraninite.

This latter work will probably be undertaken in this laboratory as opportunity may offer, together with some further experiments on some of the material already examined. It is earnestly to be hoped those possessing or in a position to procure uraninite specimens will take the trouble to examine them on the lines suggested in this paper, or if unable to do so, will kindly contribute material for examination here.

The interest in the matter is not confined merely to a solution of the composition of this one mineral; it is broader than that; and the question arises: May not nitrogen be a constituent of other species in a form hitherto unsuspected and unrecognisable by our ordinary chemical manipulations? And, if so, other problems are suggested which it is not now in order to discuss.

E.C.; Robert Ludwig Mond, 20, Avenue Road, Regent's Park, N.W.; William Shields Myers, New York; George P. Daniell Smith, 26, Colebrooke Row, Islington, N.

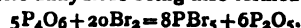
The following were elected Fellows of the Society:—Harold Alger; George Alfred Ashcroft; George James Allen; Edward Charles Cyril Baly; Thomas William Berry; Samuel Francis Burford; John Baird; J. Treeby Barratt; John Redman Bovell; John C. Chorley; William A. S. Calder; George Edward Cory; Thomas Darling; Charles E. Eastwick; Percy Elford; Lionel William Fulcher; George German, Jun.; Alfred Daniel Hall; John William Heath; Archibald Hall; John Holliday; John Walter Leather; Lionel Ludlow; Robert Lennox; Rudolf Laurentz Leffler; John Willis Marshall; Daniel McLaren, B.Sc.; Joseph Morris; William Naylor; William P. R. Newlands; Thomas Neilson; Laurence Priestley; Abhayacharan Sauyal, M.A.; Charles K. Scott; Thomas Stephenson; Walter Thorp; A. W. Winterton; John Henry Wilson; Thomas Armistead Ward; Henry White.

The following papers were read:—

68. "Phosphorous Oxide. Part II." By T. E. THORPE F.R.S., and A. E. TUTTON.

In this paper the authors continue their description of the properties of phosphorous oxide, P_4O_6 . In their first communication (*Trans.*, 1890, 553) it was stated that the oxide rapidly became red when exposed to light; they have since obtained phosphorous oxide in large, well-defined crystals, unaffected by light, by repeatedly exposing a quantity of the freshly distilled oxide to sunshine for several months at a time, and decanting the melted oxide from the red phosphorus produced. Large crystals of the oxide may also be obtained by spontaneous sublimation in a vacuum, which remain unaffected by light so long as they retain their crystalline form; but if they are melted by the warmth of the hand, and then allowed to cool to the wax like form, reddening occurs on exposure to light. Hence it appears not improbable that the permanency of the crystallised oxide is in some way connected with its crystalline character.

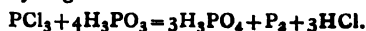
Bromine acts energetically on phosphorous oxide in a manner similar, in the end, to the action of chlorine. In a closed apparatus, however, an intermediate change occurs, crystals of phosphorus pentabromide subliming, and phosphoric anhydride being also formed—



The pentabromide is afterwards washed down by the excess of bromine, and acts on the phosphoric anhydride, the ultimate result being that products are obtained corresponding to the equation $\text{P}_4\text{O}_6 + 4\text{Br}_2 = 2\text{POBr}_3 + 2\text{PO}_2\text{Br}$.

Iodine acts more slowly than bromine, forming crystals of P_2I_4 . The interaction is best carried out in carbon bisulphide solution in a sealed tube at a temperature of 150° : $5\text{P}_4\text{O}_6 + 8\text{I}_2 = 4\text{P}_2\text{I}_4 + 6\text{P}_2\text{O}_5$.

Hydrogen chloride gas acts on phosphorous oxide, forming phosphorus trichloride and phosphorous acid: $\text{P}_4\text{O}_6 + 6\text{HCl} = 2\text{PCl}_3 + 3\text{H}_2\text{PO}_3$. A subsidiary change also occurs between the two products of the reaction, with formation of more or less phosphorus, orthophosphoric acid, and hydrogen chloride—



On distillation, a weight of phosphorus trichloride is obtained equal to that of the oxide employed.

When sulphur is heated with phosphorous oxide in a closed tube at about 160° , a most violent action takes place, the product of which is *phosphorus sulphoxide*, which is obtained in colourless, tetragonal crystals, upon sublimation in a vacuum. The crystals melt at about 102° , and the liquid boils constantly at 295° (corr.). Vapour density determinations show that the molecular formula of the sulphoxide is $\text{P}_4\text{O}_6\text{S}_4$.

It is a highly deliquescent substance, which rapidly dissolves in water, forming at first meta-, and subsequently ortho-phosphoric acid and hydrogen sulphide:

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

December 3rd, 1891.

Prof. A. CRUM-BROWN, F.R.S., President, in the Chair.

Messrs. T. M. Wyatt and Peter McEuan were formally admitted Fellows of the Society.

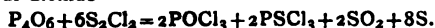
Certificates were read for the first time in favour of Messrs. Frederick Edward Adams, Town Hall, Bolton; John Edward Whitley M. Fall, Bankfield Road, West Derby, Liverpool; John C. Hewlett, 40, Charlotte Street,

$P_4O_6S_4 + 6H_2O = 4HPO_3 + 4H_2S$. It is also soluble in carbon bisulphide, from which it is again obtained upon evaporation in tetragonal prisms.

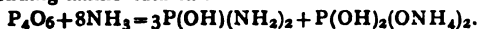
Sulphur trioxide is reduced by phosphorous oxide, the sole products being sulphur dioxide and phosphoric anhydride.

Sulphuric acid dropped upon phosphorous oxide occasions great rise of temperature; with quantities of a grm. and upwards incandescence occurs. Sulphur dioxide is liberated, and phosphoric acid formed.

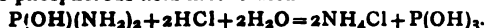
Sulphur chloride, S_2Cl_2 , also acts with violence, forming phosphoryl and thiophosphoryl chlorides, sulphur and sulphur dioxide—



Ammonia gas acts slowly in the cold, but with incandescence on warming to 30° . When ammonia is led over the oxide dissolved in ether, a white solid product is deposited, consisting of the diamide of phosphorous acid, $P(OH)(NH_2)_2$, and a small quantity of the corresponding ammonium salt—

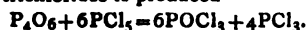


Phosphorous diamide is a white powder which is instantly dissolved by water with sufficient rise of temperature to induce incandescence. Treated with dilute hydrogen chloride solution, it evolves pure, non-spontaneously inflammable, phosphoretted hydrogen, formed by the decomposition at the high temperature of the reaction of the phosphorous acid first formed—



Nitrogen peroxide vapour oxidises phosphorous oxide in the cold to phosphoric anhydride, being reduced to nitrogen tri- or di-oxide.

Phosphorus pentachloride acts with great energy on phosphorous oxide. The action may be controlled by cooling with ice. A liquid mixture of phosphorus and phosphoryl trichlorides is produced—



Phosphorus trichloride and phosphorous oxide only interact at a temperature near the boiling-point (173°) of the latter, and in a closed vessel; under these circumstances no phosphoryl trichloride is formed, but a solid mixture of pentachloride and pentoxide of phosphorus, together with amorphous phosphorus.

Hydrogen, phosphoretted hydrogen, carbon monoxide, carbon dioxide, sulphur dioxide nitrogen, nitric oxide, cyanogen and ethylene, have apparently no action upon either cold or warm phosphorous oxide.

DISCUSSION.

Prof. RAMSAY inquired on what grounds the authors came to the conclusion that the amide described was a phosphorous and not a phosphoric compound, such as is represented by the formula $OPH(NH_2)_2$ corresponding to the formula $OPH(OH)_2$ for phosphorous acid, which latter he thought was undoubtedly a phosphoric compound. The low boiling-point and other properties of the sulphoxide described seemed to lend additional support to the view that phosphoric oxide was a compound of high molecular weight.

Dr. ARMSTRONG remarked that the conventional view that the affinity of phosphorus for oxygen was very great was somewhat disturbed by the observations now described, showing that in many cases the phosphorus and oxygen in phosphorous oxide were readily separated; it would seem that the extreme stability of phosphoric oxide was probably conditioned by peculiarity of structure.

The authors, in their reply, said that they had no special experimental proof of the constitution of the diamide formed by the action of ammonia; Prof. THORPE, however, expressed the opinion that the balance of evidence was in favour of the view that phosphorous acid is $P(OH)_3$.

69. "*Frangulin. Part II.*" By T. E. THORPE, F.R.S., and A. K. MILLER, Ph.D.

In the first communication to the Society by one of the authors, in conjunction with Mr. H. H. Robinson (*Trans.*, 1890, 38), it was concluded that frangulin had the composition $C_{22}H_{22}O_9$. This conclusion was based on analytical results alone, and it was, in fact, pointed out that the percentage yield of emodin obtained on hydrolysing frangulin agreed better with Schwabe's formula, $C_{21}H_{20}O_9$.

The authors have now prepared a larger quantity of frangulin, and have succeeded in obtaining it more nearly in a state of purity than was previously possible. They find, however, that crude frangulin contains a substance isomeric with emodin, which clings to it very persistently, and which it is very difficult to completely remove from the frangulin; they ascribe the conflicting statements of previous experimenters to the presence of this substance.

They have succeeded in proving the correctness of Schwabe's formula, $C_{21}H_{20}O_9$. Their conclusions are based not only on their more recent analyses of frangulin, but also, and in fact mainly, on the results obtained from the hydrolysis of frangulin. The two products of the hydrolysis are *emodin*, $C_{15}H_{10}O_5$, as shown in the first paper, and *rhamnose*, $C_6H_{12}O_5$. The latter substance was obtained in a crystalline form, and was identified by its chemical and physical properties and by the properties of its osazone. The percentage yield of emodin shows that one molecular proportion of frangulin yields one molecular proportion of emodin, and the difference represents one molecular proportion of rhamnose. It is thus possible to build up the formula of frangulin from its constituents, and since the result agrees with the formula deduced from the analyses of the glucoside, the conclusion is justified that frangulin has the composition $C_{21}H_{20}O_9$, and that its hydrolysis takes place in accordance with the equation: $C_{21}H_{20}O_9 + H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_5$, which was given by Schwabe as highly probable.

The substance which has been mentioned as clinging so persistently to the frangulin has been isolated, and is found to have the same percentage composition as emodin. It melts at $202-203^\circ$, and is, without doubt, the same substance which Schwabe found and described as melting at 199° . It differs from emodin also in that it crystallises in golden-yellow needles, in the greater readiness with which it sublimates, and in its reaction with alkalis. It is probably an isomeric trihydroxymethylantraquinone.

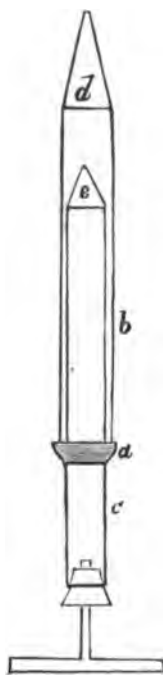
70. "*The Structure and Chemistry of Flames.*" By ARTHUR SMITHELLS, B.Sc., and HARRY INGLE, B.Sc., Yorkshire College, Leeds.

The authors have been engaged for twelve months in investigating the chemistry of flames produced by burning known hydrocarbons, and are still continuing their experiments. The publication of their results in the present form is consequent on the appearance of a paper by N. Teclu (*Journ. Prakt. Chemie*, xlv., 246), who describes the phenomenon which served as a starting-point in the authors' inquiry.

If a long glass tube be fitted by means of a cork over the metal tube of a Bunsen burner, so as to form a wider continuation of it, the flame can be caused to burn at the top of the glass tube. When the gas is turned slowly off the flame becomes smaller, and develops a sharply defined inner cone of a greenish colour; this cone ultimately becomes almost a flat disc of flame and enters the glass tube. It will, as a rule, descend at a rapid rate for some distance, then begin to oscillate and finally either detonate and light the gas at the bottom of the metal tube or else go out. If the gas supply be very carefully regulated, the flame may be got into such a state that it will descend the tube for a short distance and then re-ascend, and in this state it is very easy to see that whilst the lower cone is moving there remains at the top of the tube a steady cone of flame of a pale lilac colour. By heating the glass tube at one point, so as to increase at that point the rate of inflammation, it is possible to fix the oscillating inner cone—that is, to prevent its re-ascend. It is also possible

to effect this by narrowing the bore of the glass tube at one point, so as to diminish the rate of inflammation, i.e., to prevent the descent of the inner cone past that point. In this way it is possible to separate the two hollow cones of combustion which constitute the Bunsen flame, and to keep them any distance apart for any length of time. This permits of the aspiration of the gases from the space between the cones without any chance of admixture of outside air or of products of combustion from the upper cone.

The apparatus used by the authors in most of their experiments consisted of two glass tubes, one of which slides very easily within the other. The inner tube (c), which is the longer one, is united to the outer one by an india-rubber collar (a), through which it slides freely, and the two tubes are kept coaxial by a ring of asbestos packing (b). The projecting end of the inner tube may be fitted to a Bunsen burner, but the authors have usually led separate supplies of gas and air into the apparatus by a T-tube, instead of using a Bunsen burner, in order to



have a better control of the flame. With this apparatus a non-luminous flame is easily obtained, and the two cones can be separated in two ways. If the apparatus is arranged so that the flame is formed at the orifice of the wider tube (d), and the orifice of the narrower one (e) is 8 or 10 c.m. below it, on increasing the air supply the inner cone of flame will ultimately descend and rest upon the orifice of the inner tube. If, on the other hand, the inner tube be made to project beyond the outer one and the non-luminous flame be formed on it, then, if there be a sufficient air supply, on sliding up the outer tube it will, as it passes the flame, cleanly detach and carry up the outer cone, leaving the inner one still burning on the inner tube.

The authors have made similar experiments with flames of liquid hydrocarbons by charging air with the vapour of the liquid by passing it through a "saturator" such as is used for producing the ether-oxygen lime-light. The vapour charged air is afterwards mixed with more air, and by suitably regulating the proportions a non-luminous

flame is obtained and divided into two cones. In the case of liquid hydrocarbons, the lower cone of flame usually appears to be divided by dark spaces into several petal-like divisions which are in rapid rotation. In the case of benzene vapour the following sequence of appearances is presented:—Starting with the orifice of the inner tube, 8 or 10 c.m. below that of the outer one, a luminous smoky flame is first obtained at the latter; as air is gradually added the flame becomes less and less luminous, and an inner cone begins to develop, but before this has become non-luminous it descends to the inner tube; more air makes both it and the other cone non-luminous, and this state may be maintained. If now somewhat less air is supplied, a luminous streak appears at the tip of the inner cone, and passes right up and through the tip of the upper cone. If more air is supplied, the upper cone of the flame begins to disappear, and only the upper part of it remains; this also gradually fades away, and then there is only the lower cone left. Still more air produces a visible effect on the inner cone, the colour changing and the combustion becoming less intense until the cone rises from its seat, passes upwards and disappears. There is thus a gradual transition from the richly luminous flame to one consisting of a simple pale blue cone just on the point of extinction through excess of air.

The hydrocarbons examined by the authors were ethylene, methane, pentane, and benzene. Coal gas was also used. The gases from the regions between the two cones of flame were analysed in all these cases volumetrically or gravimetrically. The following are some of the results obtained:—

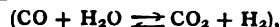
These results, which are obtained in the preliminary survey, are not quite accurate, owing to the impurity of the hydrocarbons and certain difficulties which are described in the paper. They show, however, that the products of combustion of the first cone are essentially CO_2 , H_2O , CO , and H_2 , and that the second zone is due to the combustion of the CO and H_2 with the external air.

The results are in harmony with the conclusions of Blochmann, obtained indirectly, and with the not generally known work of Dalton on the explosion of methane and ethylene with oxygen in quantities insufficient for complete combustion, which was repeated in 1861 by Kersten.

The authors point out (i.) that carbon, according to Baker's experiments, even in excess of oxygen, burns preferentially to CO , and not to CO_2 ; (ii.) that the heat of combustion of gaseous carbon to CO is probably greater than that of hydrogen to H_2O ; (iii.) that, according to Dalton, CH_4 when burnt with its own volume of oxygen gives products represented in the equation—



and they conclude that this equation represents the character of the change first taking place in the inner cone. But as the two substances CO and H_2O act upon one another—



the case is one of reversible change, and four products will result, viz., CO_2 , H_2O , CO , and H_2 .

The conditions of equilibrium of this system, according to Dixon, are expressed by the coefficient—

$$\frac{\text{CO} \times \text{H}_2\text{O}}{\text{CO}_2 \times \text{H}_2} = 4.0.$$

This is subject to certain conditions of temperature and dilution. The authors in their most reliable experiments (viz., the gravimetric ones), with ethylene and coal gas, get numbers not greatly differing from 4; but they are still engaged in studying this question.

The authors have succeeded in dividing into two cones flames produced by admixture of air with cyanogen, sulphuretted hydrogen, carbon disulphide, and decomposed ammonia (i.e., $\text{N}_2 + 3\text{H}_2$). The products of the inner cone in the case of cyanogen were found in one experi-

Substance.	C ₂ H ₄ .		CH ₄ .	C ₂ H ₆ .	C ₂ H ₁₀ .	C ₂ H ₈ .	Coal gas.		
	M.m.	M.m.	M.m.				M.m.	M.m.	M.m.
Diameter of outer tube	29	29	29	—	—	19	29	19.5	28
Diameter of inner tube	20	20	20	—	—	8	20	12	8
G (gravimetric) or V (volumetric) ..	G	V	V	V	V	V	G	V	V
CO ₂	3.8	3.6	6.8	7.0	6.5	13.1	3.8	4.2	4.8
H ₂ O	9.5	9.5	17.6	13.1	12.3	7.7	14.9	16.0	15.9
CO	15.3	15.6	4.5	7.9	9.5	5.0	10.2	8.8	7.1
Hydrocarbons	0.8	1.3	—	—	—	0.6	—	—	—
H ₂	9.5	9.4	3.9	5.4	5.8	0.64	10.9	9.3	7.7
N ₂	61.1	60.6	67.2	66.2	65.6	73.1	60.3	62.0	64.4

ment to consist of CO and CO₂ in the proportion of 2 vols. of the former to one vol. of the latter.

Professor Smithells is continuing the experiments with a view of elucidating the following points:—

- (i.) The influence of differences of diameter of the tubes and rates of efflux on the fractional combustion.
- (ii.) The exact composition of the interconal gases in the case of hydrocarbons, and also of mixtures of CO + H₂, so as to ascertain if, and in what way, the coefficient—

$$\left(\frac{\text{CO} \times \text{H}_2\text{O}}{\text{CO}_2 \times \text{H}_2} = 4 \right)$$

varies with the composition of the gases and other conditions.

- (iii.) The composition of the interconal gases from hydrocarbon flames whilst carbon is being liberated, so as to ascertain whether the luminosity of flame is due to simple decomposition of hydrocarbons by heat, to preferential combustion of hydrogen, to partial decomposition, or to other change.
- (iv.) The exact nature of the flame of cyanogen, so as to ascertain what governs the proportions of CO and CO₂ formed in the inner cone.
- (v.) The manner in which the partition of oxygen takes place in the inner cone between C and H, H and S, C and S, so as to obtain information as to the affinities of C, H, and S for oxygen.
- (vi.) The spectroscopic appearances of the flames.

DISCUSSION.

Professor THORPE after expressing regret that time did not permit of the discussion of the numerous interesting questions which had been raised, referred to Professor Smithells's remark, that the books failed to notice the fact that carbonic oxide was produced on partial combustion of methane. He pointed out that Mr. Thomas, several years ago, made a special study of this question, having been led to do so by the observation that in cases of undoubted marsh gas explosions in coal mines the men killed often exhibited an appearance suggestive of carbonic oxide poisoning. Mr. Thomas found that carbonic oxide and hydrogen were regular products of the incomplete combustion of marsh gas. (Cf. "Coal Mine Gases and Ventilation," by J. W. Thomas. Longmans and Co., 1878. Also *Iron*, 1875).

(To be continued.)

PHYSICAL SOCIETY.

December 4th, 1891.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

Messrs. P. L. Gray, A. Anderson, H. Davey, L. W. Fulcher, H. H. Hoffer, and W. Watson were elected members.

A paper on "A Permanent Magnetic Field" was read by Mr. W. HIBBERT, A.I.E.E., F.I.C.

The author had noticed the approximate constancy of an "aged" bar magnet, and he obtained still greater constancy by attaching pole-pieces to a bar magnet, of such

a shape as to give a nearly closed circuit of small "magnetic resistance." The pattern now described consists of a steel rod 1 inch diameter and about 2½ inches long, with a cast-iron disc 4 inches diameter and ½ thick, fixed at one end; the other end is fitted in a hemispherical iron shell which surrounds the bar and comes flush with the upper surface of the disc. An annular air space, less than 1/16 wide, is left between the cylindrical surface of the disc and the inside of the shell; and when the bar is magnetised a strong magnetic field exists in this space. To use this field for producing electro-magnetic impulses, a coil of wire is wound, in a shallow groove, on a brass tube which can slide easily through the annular space, thus cutting all the lines. The tube is allowed to fall by its own weight, a neat trigger arrangement being provided for effecting its release.

The instrument exhibited had 90 turns of wire in the coil, and the total magnetic flux across the air space was about 30,000 C.G.S. lines. A large electro-magnetic impulse is therefore obtainable even through resistances as great as 10,000 ohms. Tests of three instruments show that there has been practically no magnetic decay in seven months. The author therefore considers them satisfactory, and is prepared to supply them as magnetic standards. To facilitate calculations the number of lines will be adjusted to a convenient number, say, 20,000 or 25,000.

Several uses to which the instruments are well suited are mentioned in the paper, and a simple way of determining permeability by the magnetometer method is described.

Mr. BLAKESLEY thought the name given to the instrument was inappropriate, for it really gave a constant impulsive E.M.F.

Dr. SUMPNER said the constancy of the sensibility of d'Arsonval galvanometers was a measure of the constancy of magnets having nearly closed circuits. Such instruments, in use at the Central Institution, had remained unchanged for several years.

Prof. S. P. THOMPSON admired Mr. Hibbert's instrument, and thought it would be very useful in laboratories. Standard cells, he said, were not always reliable, and condensers were the most unsatisfactory of electrical standards. On the subject of permanency of magnets, he said that Strouhal and Barus found that magnets with nearly closed circuits were most constant, and that, to give the best results, the hardness of the steel should be less the more closed the circuit. Mr. Hookham had also found that by using a nearly closed circuit and reducing the strong magnetisation by about 10 per cent, great constancy could be obtained.

Some years ago, he (Dr. Thompson) had tried the effect of ill-treatment on magnets, and observed that touching or hitting a magnet with non-magnetic material had little effect, whilst similar treatment with iron or magnets affected them considerably. Suddenly removing the keeper of a magnet tended to increase the magnetism, whilst putting a keeper on suddenly had the reverse effect. Strouhal and Barus had also investigated the temperature coefficient of magnets, and found that this might be reduced by subjecting the magnet to rapid changes of temperature after the first magnetism, and then remagnetising.

Mr. W. WATSON enquired what was the percentage fall in strength of Mr. Hibbert's magnets. The bars used in magnetic surveys had been tested frequently, and they lost about 0.5 per cent in six months.

The PRESIDENT asked what was the temperature coefficients of the magnets described in the paper? Mr. Evershed, he said, thought it was between 0.01 per cent and 0.05 per cent for ordinary magnets. He thought the instrument shown by Mr. Hibbert would be of immense value if the magnet was really permanent. By it ballistic galvanometers could be readily calibrated, and, when combined with a resistance bore, it could also be used as a standard for current; for since the constant of a ballistic galvanometer for quantity can be determined from its constant for current, if the periodic time be known, conversely, that for current can be found from the constant for quantity. In some instances this would be of great use. Speaking of the temperature coefficient of condensers, he said that, in some cases, the specific inductive capacity of dielectrics diminished with rise of temperature, whilst in others it increased.

Mr. HIBBERT, in reply, said he found the temperature coefficient of his magnets to be roughly about 0.03 per cent, but he had not investigated the matter very carefully. In making his measurements no correction had been made for the variation of capacity of his condenser with temperature.

Mr. WALTER BAILY, M.A., took the Chair, and

The PRESIDENT communicated "A Note on Rotatory Currents."

The subject, he said, was probably familiar to most persons present, for it had been frequently referred to in the scientific papers. Alternate currents could be obtained from an ordinary direct current dynamo by making contact with two points in the armature, say by connecting these points to insulated rings on the shaft, and using extra brushes. A direct current motor, similarly treated, transforms direct currents into alternating currents or into mechanical power. If two pairs of points in the armature be selected, situated at opposite ends of two mutually perpendicular diameters, then two alternating currents, differing in phase by 90°, can be obtained; and by choosing suitable points in the armature, two, three, or more currents, differing in phase by any desired angles, can be produced. In ordinary motors, the connections for doing this would be troublesome, but the Ayrton and Perry form, which has a stationary armature, lends itself readily to this purpose, for contact can be made with any part of the armature with great facility. A motor of this kind was exhibited, in which contact was made with four equidistant points on the armature. On connecting opposite points through fine platinum wires, and running the motor slowly, the wires glowed alternately, one being bright whilst the other was dark, and *vice versa*, thus demonstrating the existence of two currents in quadrature. When the four points on the armature were joined to the four corners of a square of platinum wire, the wires became incandescent in succession, the glow appearing to travel round the square, and suggesting the idea of rotatory currents. A Tesla alternating current motor was also driven by two currents differing in phase by 90° obtained from the armature of the Ayrton and Perry direct current motor above mentioned.

The ease with which currents differing in phase by any amount can be obtained from such a motor led the author to investigate theoretically the case of two circuits connecting opposite ends of two diameters inclined at any angle α . Calling the currents in these circuits at any instant, A_1 and A_2 , he had found that—

$$A_1 = 2nE_0 \sqrt{(r_2 + \rho_2^2)^2 + \rho^2(\frac{\pi}{2} - \alpha)^2 - 2(r_2 + \rho_2^2)\rho(\frac{\pi}{2} - \alpha) \cos \alpha} \\ (r_1 + \rho_1^2)(r_2 + \rho_2^2) - \rho^2(\frac{\pi}{2} - \alpha)^2 \cdot \sin(\phi + \psi),$$

where—

n = number of turns on armature per radian;
 E_0 = maximum E.M.F. per convolution;
 ρ = resistance of armature per radian;
 $\dot{\phi}$ = angular velocity of rotation;
 r_1 = resistance of external circuit in which current A_1 passes;
 r_2 = resistance of external circuit in which current A_2 passes; and—

$$\tan \phi = \frac{\rho(\frac{\pi}{2} - \alpha) \sin \alpha}{r_2 + \rho_2^2 - \rho(\frac{\pi}{2} - \alpha) \cos \alpha}$$

A similar expression, in which r_1 is written for r_2 , and r_2 for r_1 , gives the value of A_2 .

The phase angle between the currents is given by $\tan(\phi + \psi)$

$$= \frac{(r_1 + \rho_1^2)(r_2 + \rho_2^2) - \rho^2(\frac{\pi}{2} - \alpha)^2}{(r_1 + \rho_1^2)(r_2 + \rho_2^2) + \rho^2(\frac{\pi}{2} - \alpha)^2 - (\rho_1^2 - \alpha)(r_1 + \rho_1^2) \cdot \tan \alpha} \cdot \tan \alpha.$$

The expression for ϕ shows that the phase of the current in circuit A_1 is independent of the resistance r_1 . On the other hand varying r_2 alters ϕ .

It was also pointed out that $\tan(\phi + \psi)$ is generally greater than $\tan \alpha$.

Prof. J. PERRY, F.R.S., read a paper on "Struts and Tie-rods Laterally Loaded." He pointed out that in the case of struts a slight want of straightness may considerably reduce the breaking load. Even if a strut be originally straight and the thrust properly distributed, its weight usually produces lateral loading and consequent bending. Similarly, centrifugal force produces lateral loading in connecting rods. For some years the author has given his students practical examples of struts and tie-rods to work out, taking into account the effect of lateral loads. The chief results obtained, together with a general treatment of the whole subject, are embodied in the paper. Where the curves of bending moment and the deflections due to lateral loading can be easily developed by Fourier's Series, solutions can readily be found.

Simple cases of uniformly loaded struts and tie bars have been fully worked out, and also the case of locomotive coupling rods. In one problem on the latter subject a rectangular cross section was chosen and the proportions of depth to breadth determined so as to make the rod equally strong in the two directions when running at various given speeds. With cranks 12 inches long, the results show that at a speed of 390 revolutions per minute the ratio of depth to breadth must be infinite so as to give equal strength, so great is the influence of the lateral loading due to centrifugal force when combined with the thrust. Horizontal tie-rods loaded by their own weight have been investigated, and the tensions required to neutralise compression due to bending determined. A steel bar was used as a strut, with a thrust of 1500 lbs. The maximum stress due to bending by its own weight alone was 816, and on applying the thrust the maximum stress was raised to 23,190, or about twenty-six times that due to lateral loading alone. More complex cases have also been treated, the results of which are given in the paper.

OBITUARY.

PROFESSOR STAS.

THE chemical world—indeed, we may say Science in general—has just experienced a severe blow by the death of Professor Stas, of Brussels. Although, perhaps, little known to the outside public, the deceased *savant* has earned undying honour and gratitude by his prolonged and splendid researches on the atomic weights of many of the elements. His laborious accuracy, his acuteness

in detecting possible sources of error, his fertility of resource in their elimination, and his conscientious determination to be satisfied with nothing less than unquestionable truth, will remain a model for all generations. We purpose giving particulars next week.

NOTICES OF BOOKS.

An Introduction to Chemical Theory. By ALEXANDER SCOTT, M.A., D.Sc. London and Edinburgh: A. and C. Black.

OF elementary text-books, which are occupied almost exclusively by the enumeration of facts and the description of experiments, we have had of late years a plethora. But works which aim at bringing the results of observations and experiment into harmonious connection have been scarce indeed. Now, when even zoology and botany have left behind them the mere descriptive stage, it is surely an opprobrium for chemistry to linger in the rear.

The author notices with due regret that "those who have had to teach the elements of both chemistry and physics to the same classes of students usually find the progress of their pupils more rapid and satisfactory, for a time, at least, in the latter subject."

This difference he ascribes, with great probability, to the smaller number of facts, apparently disconnected, which are required in physics before they can be grouped together and built up deductively. His undertaking, therefore, is most commendable, and we believe that it will contribute to a wider and clearer understanding of chemical theory. Dr. Scott lays no claim, as regards the work before us, to either originality or completeness; but matter which is scattered through the scientific journals and the transactions of the learned Societies requires to be collected and often explained before it can be available to the student.

In accordance with the destination of his book, the author confines himself within the boundaries of what may be regarded as fairly established, leaving speculative subjects for the study of another class of readers.

He arranges his subject-matter under the headings of The Constitution of Matter; Atomic Weights; Molecular Weights; Classification of Elements; Classification of Compounds, Acids, Bases, Salts, and Carbon Compounds; Abnormal Vapour-densities and Dissociation; Physical Properties of Compounds; Thermo-chemistry; Chemical Change; Solution and Electrolysis.

Dr. Scott recognises that the laws of Boyle, Charles, and Avogadro are true only to a limited extent. Prout's law is discussed at some length, mainly in order to throw light upon the determination of atomic weights. He considers that much may be said for this supposed law, if for the atomic weight of hydrogen we substitute $\frac{1}{8}$ part of the atomic weight of oxygen.

In considering the classification of the elements, he accepts the Newlands-Mendeleeff system, with certain reservations.

As regards formulæ and symbols, the author protests against their common use as a kind of shorthand to express indefinite quantities of the substances in question. This practice is very common in the abridged text-books now so abundant. He insists that each term of an equation should refer to a definite number of molecules, and not of atoms as such.

Our ordinary notation, the author thinks, is sufficient for inorganic chemistry; but for organic compounds the case is different. Here, however, occur two questions:—Does not the chemistry of silicon closely approximate to that of carbon? and, again, Can we suppose the atoms in each individual molecule arranged on a plane? Into this latter question the author enters to some extent when expounding the researches of Le Bel and Van't Hoff.

In treating of solution, Dr. Scott decidedly leans to the

"osmotic pressure" or "dissociation theory," and considers that the burden of proof should be laid upon the advocates of the "hydrate theory."

We can most strongly recommend this book to the notice of teachers as a guide for the studies of their more advanced pupils. We are compelled to add—of teachers who are at liberty to follow their own judgment, unfettered by any "syllabus."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxliii., No. 22, November 30, 1891.

On Boron Phosphides.—A. Besson.—The author mentions a curious reaction of boron phosphide. The product of its limited oxidation by means of dilute nitric acid, on evaporation to dryness, presents the aspect of nacreous laminæ, which, if dissolved in luke warm water, give with ammonia in excess a white gelatinous precipitate. There appears to be formed under these conditions a peculiar phosphoboric acid, the ammoniacal salt of which is sparingly soluble.

Bromo-derivatives of Methyl Chloride.—A. Besson.—The monobromo-compound, CH_2BrCl , is a colourless liquid, which distils without decomposition at 68° with an odour resembling that of chloroform. It does not solidify at -55° . It becomes slowly coloured on exposure to air and light, with loss of bromine. Its specific gravity at $+15^\circ$ is 1.90; its vapour density taken with Hoffmann's apparatus in watery vapour is 4.72; theory demands 4.50. The corresponding dibromo compound, CHBr_2Cl , has been previously obtained by Jacobsen and Neumeister in the action of potassa on a chlorobromic aldehyd. These chemists ascribe to the compound a boiling-point between $123-125^\circ$. This boiling-point must be lowered by several degrees so as to lie between $117-119^\circ$. It solidifies at -32° , its vapour density (taken in the vapour of aniline) is 7.18, the theoretical value being 7.25.

A Modification of M. Berthelot's Calorimetric Bomb, and on the Industrial Determination of the Calorific Power of Combustibles.—Pierre Mahler.—This memoir does not admit of useful abstraction.

The Fixation of Free Nitrogen by Plants.—Th. Schloesing Fils and Em. Laurent.—The author's results are that there are inferior green plants which are able to obtain gaseous nitrogen from the atmosphere. Under the conditions of their experiments bare soils, oats, mustard, cress, asparagus, have not fixed free nitrogen in measurable quantities. It has been once more verified that under the same conditions peas are capable of fixing large quantities of atmospheric nitrogen.

Ammonia in the Atmosphere and in the Rains of a Tropical Region.—V. Marciano and A. Muntz.—The air in the tropical region studied (near Caracas, in Venezuela), is, contrary to expectation, less rich in gaseous ammonia than that of temperate climates. There is an abundant formation of nitric acid in the air of tropical countries, so that the ammonia combining with this acid ceases to be gaseous and forms crystalline dust.

Influence of the Solar Rays upon the Ferments met with on the Surface of Grapes.—V. Martinand.—It is found that grapes growing on the lower shoots of the vines yield a very large quantity of *Saccharomyces*, among which *S. apiculatus* predominates. On grapes from the middle height and from the summit of the vines, the ferments are very few in number. *S. ellipsoideus*, which is the most useful yeast for the fermentation of wine, is the more plentiful the less intense are the solar rays.

Bulletin de la Société Chimique de Paris.

Series 3, Vol. vi., Nos. 6 and 7.

A New Acetylenic Carbide, α -Naphthylacetylene.—A. J. Leroy.—This compound is a colourless liquid boiling at $143-144^\circ$ under a pressure of 25 m.m. Its composition is shown by the formula $C_{10}H_7-C\equiv CH$. It precipitates Báhal's reagent (alcoholic silver nitrate).

Organic Molecular Combinations obtained by Fusion (Aromatic Hydrocarbons).—Leo Vignon.—If we have a mixture of two definite fusible solids, which do not react with each other chemically in the ordinary sense of the word, and if we determine their melting-point, we find that it generally differs from the mean of the melting-points of its two components. This has been observed in case of mixtures of metals, fusible salts, and fatty acids. The author, experimenting upon a great number of bodies of definite and varied functions, has observed the same phenomenon. From the totality of the facts it results that the systems examined as regards their fusibility may be distinguished into two groups: A, mixtures without anthracene; and B, those containing anthracene. The author represents the characters of the two classes graphically. The melting-point of any given anthracenic system increases regularly with the proportion of anthracene, and is always a little higher than the calculated melting-point.

Action of Chlorine upon Certain Acetones of the Fatty Series.—Demetrius Vladesco.

On Certain Nitro-derivatives of Dimethylate Ortho-Anisidine.—E. Grimaux and E. Lefevre.—These two memoirs do not admit of useful abstraction.

Production of Cuprous Acetylene by the Action of Acetylene upon Copper in Presence of Ammonia.—M. Kuntzmann.—This note requires the accompanying cut.

MISCELLANEOUS.

Whitaker's Almanack.—We have received from the publishers a copy of "Whitaker's Almanack" for 1892. The most important alterations to be noted in the contents of this valuable work are to be found in the enlargement of its sections. Additional space has been allotted to educational matters, and a separate article dealing with educational progress and occurrences is given for the first time. Agricultural education also forms the subject of a separate article. An article on our present ocean mail supplies a convenient record of the rise, progress, and best achievements of the great lines of ocean steamers. Naval gunnery and a synopsis of the results of the census are also amongst the subjects separately treated. Every page and almost every line of the work has been corrected, and as nearly as possible brought up to the date of issue. In many instances the changes wrought during the brief interval of a single year are so numerous that scarcely a line of the section in which the subject is dealt with remains unaltered.

The New "Methylated Spirit."—Not the least of the difficulties encountered by British industrial chemists in competing with foreign rivals has been the lack of cheap alcohol. To meet this difficulty the sale of "methylated spirit" was permitted,—a mixture, as most of our readers know, of alcohol with impure wood spirit. This liquid was in many cases further contaminated with shellac, an addition objectionable to all consumers save the varnish-makers. Still the methylated spirit when free from resinous matter was no small boon, and was preferred, *e.g.*, by photographers to pure ethylic alcohol. The powers that be, however, were afraid that the article was too good for use in the arts, and have therefore enacted that it must be polluted by a further addition of coal naphtha! The alleged reason for this step in the wrong direction is that

the methylated spirit was drunk by workmen and others to the injury of the revenue and the promotion of intemperance. The new preparation fills photographers and many chemical manufacturers with dismay. If such spirit comes in contact with water or any aqueous liquid it is at once rendered turbid and unfit for use. The hope that it will not be drunk is fallacious. We have known of hands at chemical works—seasoned toppers—who would even toss off a "tot" or *petit verre* of the coal naphtha itself! If the heads of the Revenue really wished to make the spirit undrinkable they should have prescribed the addition of Dippel's animal oil. A mere trace of this liquid, without interfering with the legitimate uses of the spirit, renders it so loathsome to smell and taste that no one would dream of drinking it. This is no untried expedient; it is one of the legalised additions used in Germany for "denaturising" alcohol.

MEETINGS FOR THE WEEK.

TUESDAY, 22nd.—Photographic, 8.
WEDNESDAY, 23rd.—Geological, 8.

TO CORRESPONDENTS.

G.—A book by the Editor on the "Manufacture of Beet-root Sugar in England" was published some years ago by Messrs. Longmans.

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THE CHEMICAL NEWS.

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THE DENSITIES OF SULPHURIC ACID SOLUTIONS.

By SPENCER U. PICKERING, F.R.S.

A SHORT time ago Mr. H. D. Richmond (*Four. Soc. Chem. Ind.*, 1890, p. 479), made use of my determinations of the densities of sulphuric acid solutions (*Chem. Soc. Trans.*, 1890, pp. 139—158), to construct a very full table of the values for strong solutions at 15° C. Not long afterwards Prof. Lunge (*Four. Soc. Chem. Ind.*, 1890, p. 1017), feeling hurt, apparently, that anyone else's determinations should have been preferred to his own, published a paper—to which my attention has only recently been directed—in which he sought to cast obloquy on the accuracy of my values; but as the method which he selected for doing so consisted in making misrepresentations so gross that no one who read my work would have paid the least heed to them, I should not have thought it worth while to say anything about it were it not that Mr. Richmond's labour runs the risk of being neglected by those for whose benefit it was intended, but who might not be inclined to examine the dry data from which he obtained his material.

Mr. Richmond says:—"The recent work of Pickering has placed at our disposal a series of determinations which is, without doubt, the most complete yet published, and from them I have calculated a table, giving for each 0.0001 of specific gravity the corresponding percentages of sulphuric acid. My reasons for preferring the determinations of Pickering to all other observers, are the precautions taken to observe accuracy, and the large number of determinations made, he having made nearly as many determinations as all the other observers put together." Mr. Richmond's table gave the values for 15°; but instead of taking these from my table, which contained values for this same temperature as deduced from observations made at 8°, 18°, 28°, and 38°, he deduced them afresh from the observations at these latter temperatures, and it is satisfactory to find that he obtained practically the same values as I did; he says:—"my figures on comparison agreed almost absolutely with those in his (Pickering's) table, in no case was there a difference of more than 0.00002 in the density; the accuracy of the table, then, is beyond doubt."

In order to cast doubt on this accuracy Prof. Lunge boldly states that I maintain that the percentage strength of my acid was known to an impossible degree of nicety—ten times greater than that to which I said it was known—and, moreover, that I pretend to have obtained this accuracy by analysis, whereas I was most careful to point out that I did not rely on analysis, and that no analysis would have given me even such accuracy as that which I did obtain.

Prof. Lunge says:—"The enormous amount of his (Pickering's) observations, and the seemingly stupendous accuracy of those, indicating *thousandths* of a per cent of H₂SO₄ in the acid, may possibly make them appear more trustworthy than ours to those who have not worked in the same field. But I cannot for one moment acknowledge this conclusion. Hundreds of tests made by myself with the greatest possible care and calibrated vessels and corrected weights, with constant checkings and re-checkings, have proved to me that estimations of strong sulphuric acid are already *very* good if they do not differ from one another by more than one unit in the first

decimal per cent, and that the utmost accuracy attainable, but most certainly not attained by the majority of workers, is ± 0.05 per cent. If Prof. Pickering maintains (*Chem. Soc. Trans.*, 1890, p. 73) that his percentages are accurate to ± 0.001 , this impossible assumption is to my mind from the outset a reason for distrusting the accuracy of his figures altogether, and I believe that this impression will be conveyed to others as well who take the trouble of looking at the very tottering foundations of that seemingly stupendous accuracy. . . . All his hundreds of observations are founded upon the analysis of a sample of pure sulphuric acid. . . . The fundamental analyses were not made by Prof. Pickering himself, but by Mr. Crompton. . . . Now these estimations of Mr. Crompton's vary between 99.704 and 99.962 per cent, that is, to the amount of 0.26 per cent, and yet Prof. Pickering does not hesitate to assert that the percentages of his acids . . . are accurately known to the third decimal per cent." In his recently published book ("Sulphuric Acid and Alkali"), Prof. Lunge reiterates these views, and refers to the passage here quoted; and again, when speaking of my freezing-point determinations (p. 134) he makes a similar remark, saying:—"But we must remark that the apparent extreme accuracy of the estimations is quite illusory, since, even with the best methods known and the greatest skill, a *reliable* estimation of the strength of sulphuric acid can only be made up to the first decimal of the percentage amount, the second decimal being uncertain by ± 5 , whilst in that memoir four decimal places are given! The third decimal of the thermometric estimations must be equally uncertain."

Some of these objections have already been raised by Mr. Sydney Lupton, and it is tedious work to have to correct for a second time the blunders made by critics who decline to read the papers which they attempt to criticise. In the present case, indeed, it requires some self-restraint on my part not to accuse the critic of a wilful misrepresentation of statements, and a perversion of the facts of the case; nowhere, either on p. 73 (*Chem. Soc. Trans.*) or elsewhere, have I maintained that the percentages quoted were accurate "to 0.001," nowhere have I asserted, either with or without hesitation, that they were known "to the third decimal per cent." On the contrary, ± 0.01 per cent is the figure printed most clearly on p. 73, previously also on p. 72, and subsequently on p. 85, in the form of 1-10,000th. On pp. 72 and 73 there are eighteen lines, and, again, on p. 338 thirteen lines, devoted to inform readers that the results of Mr. Crompton's analyses were not taken for determining the strength of the acid, but that a method "more reliable than any analysis" was found and accepted, this method being based on the fact that the pure acid must have a higher freezing-point than an acid with excess of either water or anhydride, and the superior accuracy obtained by employing such a method is mentioned again on p. 84 as being the first of the three special advantages which my determinations offered for constructing a table of densities; there is also a further allusion on the same page to the fact that this method, and not the analytical one was used, and I re-stated this fact in my answer to Mr. Lupton (*Phil. Mag.*, 32, p. 95).^{*} What excuse, then, can Prof. Lunge have for the assertions which he has made? His misrepresentations are so glaring and so confidently repeated that it seems scarcely possible to attribute them to mere carelessness on his part. Even the *relative* accuracy of the strength of the solutions—the only accuracy which was of importance for the immediate purposes of my work, as I have so often pointed out (*vide Chem. Soc. Trans.*, pp. 73, 85; *Phil. Mag.*, 32, p. 85)—does not correspond with his 0.001 per cent, for it

* For the purposes of differentiation the percentages taken were not corrected in accordance with the results given subsequently by the freezing-point method, because the correction would have had no appreciable effect whatever on the differential values. But this has nothing to do with Prof. Lunge's remarks, for he is speaking of the density table, for the construction of which the corrected values were taken.

* All italics are Prof. Lunge's.

was "one unit in the fourth decimal place of the percentage."

I may mention that I never impugned the accuracy of, or even alluded to, Prof. Lunge's determinations, though I believe that the three advantages possessed by my determinations for the construction of a table is not possessed by either his or those of any other experimentalist. Prof. Lunge does not seem to have understood these advantages, but by laying such stress on the fact that no analysis will suffice to determine the strength within ± 0.05 per cent, he unconsciously brings forward a strong argument in favour of the accuracy of my results, which were based on a non-analytical method capable of five times this amount of precision. The other advantages for the construction of a table afforded by my determination were that they were very numerous, and were made with solutions of very nearly round percentage values. Their great number also, by affording data for the accurate determinations of the rate of change, diminished the chances of errors in the process of interpolation necessary in constructing a table.

It seems ridiculous to have to point out a second time (see *Phil. Mag.*, 32, pp. 94, 103), that the quotation of a value to a given decimal place does not mean that it is known with certainty, either as to its actual or relative magnitude, to that decimal place, and it seems, still more ridiculous to have to call the attention of critics again to the fact that the probable error of the mean of a number of analyses is not the same as the extreme difference between any selected two of the individual results.

Prof. Lunge makes some other remarks which bear on my work, and they all show as much carelessness as those already discussed.

On page 114 there is a statement which is calculated to imply the existence of a great discrepancy between Thomsen's and my own heat determinations:—"The heat of neutralisation of 1 molecule H_2SO_4 by 2 molecules NaOH, in the presence of 400 molecules of water, is given by Thomsen = 31,380 cal. Pickering (*Journ. Chem. Soc.*, 1889, p. 323) states it only 28,197 cal." As a matter of fact I never determined the heat of neutralisation of the acid, and never made any statement as to its value in the presence of 400 H_2O being different from that given by Thomsen; on the contrary, I showed that if we accepted Thomsen's value, and from it and my own results of the heat of dilution of the acid (Thomsen's were not extended far enough for this purpose), deduced its probable value for infinite dilution, we got 28,197 cal.—a result which is of considerable importance, inasmuch as this value agrees within experimental error with the normal values obtained in the cases of most other acids.

On page 126 Prof. Lunge mentions my having isolated the tetrahydrate of sulphuric acid (f. p. -25°), which contains 57.66 per cent H_2SO_4 , and says that "by adding a little water or sulphuric acid its freezing-point is at once lowered to -70° ," a statement which would make anyone sceptical as to the correctness of my observation. The fact is that a gradual lowering of the freezing-point occurs by the addition of acid or water, and only attains -70° when the total percentage of acid present is reduced to about 39 or raised to 71.

Lastly, on page 126 he says "a third hydrate, $SO_4H_2 \cdot 2H_2O$, is assumed, because on diluting strong vitriol with water down to this point the largest contraction, viz., from 100—92.14 vols. take place." It has, however, been known for some time that the position of maximum contraction varies with the temperature, and a reference to pp. 84 or 148 of my paper would have shown Prof. Lunge that at 18° it does not occur at 73 per cent, the composition of the dihydrate, but at 68 per cent.

Prof. Lunge's reference to the contraction occurring on mixing sulphuric acid with water led me to calculate from his own results (Lunge and Isler, *Zeit. Angew. Chem.*, 1890, p. 131) the values for these contractions for different strengths of acid, and the values obtained led me to a somewhat unexpected conclusion, namely,

that the accuracy of his determinations is by no means very great. On differentiating the values we get a series of numbers, $\frac{dC}{dp}$, which exhibit irregularities sufficiently

large to be apparent on a superficial inspection, and which compare very unfavourably with those deduced from my own determinations (*Chem. Soc. Trans.*, p. 148), of which I have here given a few for the purpose of

Contraction in c.c. on the Formation of 1 grm. of
Sulphuric Acid Solutions.

LUNGE.			PICKERING.		
P.c. Acid.	Contr.	$\frac{dC}{dp}$	p.	C.	$\frac{dC}{dp}$
100	0		91.025	0.03723	
95.88	0.01946	-0.00472	90.046	0.04014	-0.00298
90.85	0.03760	-0.00359	89.031	0.04293	-0.00275
88.30	0.04541	-0.00306	87.958	0.04566	-0.00255
83.38	0.05508	-0.00197	87.036	0.04779	-0.00232
73.60	0.06201	-0.00071	85.958	0.05016	-0.00220
69.70	0.06235	-0.00009	84.979	0.05180	-0.00167*
66.65	0.06304	-0.00023	83.566	0.05403	-0.00158*
63.14	0.06145	+0.00045	82.982	0.05484	-0.00139
59.03	0.06147	0	81.985	0.05602	-0.00119
55.15	0.05982	+0.00043	81.093	0.05695	-0.00104
51.38	0.05776	+0.00028	79.985	0.05791	-0.00086
46.94	0.05744	+0.00007	78.990	0.05862	-0.00072
42.67	0.05410	+0.00078	78.254	0.05911	-0.00066
38.57	0.05216	+0.00047	75.957	0.06034	-0.00054
35.15	0.05021	+0.00057	74.004	0.06091	-0.00029
31.15	0.04562	+0.00115	72.023	0.06135	-0.00022
27.42	0.04194	+0.00099	70.098	0.06158	-0.00012
23.61	0.03906	+0.00076	68.101	0.06165	-0.00004
20.08	0.03435	+0.00133	66.133	0.06156	+0.00005
15.60	0.02792	+0.00166	64.891	0.06145	+0.00009
11.76	0.02211	+0.00152	64.112	0.06135	+0.00014
6.18	0.01234	+0.00175	62.041	0.06095	+0.00019
3.31	0.00703	+0.00185	59.989	0.06037	+0.00028
1.85	0.00422	+0.00193	57.889	0.05984	+0.00025
0.91	0.00213	+0.00222	55.877	0.05921	+0.00031
0	0	+0.00234	53.896	0.05849	+0.00036

* These values are wrongly quoted in the Table at p. 148 of the *Chem. Soc. Trans.*, 1890, a miscalculation of the volume of one solution having been made. This should be 0.562069, instead of 0.562169 as there given; the density from which this value is deduced is given correctly on p. 139.

comparison. The magnitude of the errors in Prof. Lunge's values for $\frac{dC}{dp}$ must, I think, be taken as indicating the existence of errors of no less than 0.0005 or 0.001 in his values for the contractions; an error of 0.001 in the contractions represents from 0.001 to 0.0035 in his density determinations, or 0.23 in the relative percentage strengths of his acids, and must negative any claims to real accuracy which his determinations might have been supposed to possess.

THE SUPPOSED COPPER NITRIDE.

By P. L. ASLANOGLU.

In the *Phil. Mag.*, 3., xix., 100, July—December, 1841, W. R. Grove, M.A., F.R.S., refers to some of his electrolytical experiments, that when a piece of metallic copper is connected with the positive pole of a battery in a solution of ammonium chloride, and the negative pole of the battery is connected with a platinum plate which also dips into the solution, after a time the liquid becomes blue, and a chocolate coloured nitride appears to be formed of specific gravity 5.9, and 5 grains of the substance give off 0.107 inch of nitrogen gas when heated, leaving copper. T. E. Thorpe,* Ph.D., F.R.S., and H. Watts,† B.A., F.R.S., F.C.S., refer to the above.

I have repeated the above experiment several times, and found the specific gravity of the substance to be 5.6. I have tested for nitrogen by Dumas's method, and obtained a negative result, therefore I suggested analysing the substance as an oxide of copper, and out of several experiments I have chosen the three following:—

Found percentages in grms.—

	I.	II.	III.
Oxygen	7.8262	7.7954	7.6551
Copper	91.8202	90.5482	88.6781
	99.6464	98.3436	96.3332

and taking the mean of the three experiments—

Oxygen	7.7589
Copper	90.3488
	98.1077

which approximately correspond to the formula of Cu_3O , being—

Oxygen	7.8048
Copper	92.1951
	99.9999

	Theory.	Found.	Difference.
Oxygen	7.8048	7.7589	0.0459
Copper	92.1951	90.3488	1.8463
	99.9999	98.1077	1.8922

With my experiments the copper found comes lower than that of the theory, the cause being that when heating the substance in a boat, testing for oxygen, some of the heated substance adheres to the sides of the tube, consequence of low percentages for copper.

Although by looking into the substance itself you cannot detect any metallic copper, yet on applying the elutriation system you can plainly see at the bottom of the agate mortar traces of metallic copper. Therefore the substance was covered with a saturated solution of

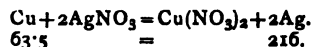
silver nitrate for the purpose of separating the oxide of copper from the metallic copper, and thus estimating the right formula of the substance:—



We let it stand in the cold for twelve hours and filter.

The residue $2\text{Ag} + \text{Cu}_2\text{O}$ is dissolved with HNO_3 , and we precipitate the silver by HCl , and filter. The residue is AgCl , and the filtrate $\text{Cu}(\text{NO}_3)_2 + \text{HNO}_3$.

The AgCl is washed, dried, weighed, and determined as with the chlorides.



$$\begin{array}{ccc} \text{AgCl} & \text{Ag} & \text{AgCl} \\ 143.5 & : 108 & :: 1.587 : x. \end{array}$$

$$x = \frac{1.587 \times 108}{143.5}.$$

x = amount of silver.

$$\frac{\text{Ag}}{216} = \frac{\text{Cu}}{63.5}.$$

$$\therefore 216 : 63.5 :: x : x.$$

$$x = \frac{x \times 63.5}{216} = \text{amount of metallic copper contained in}$$

the original substance.

Found metallic copper—

$$\begin{array}{l} \text{I. } 29.398 \\ \text{II. } 29.142 \end{array}$$

The filtrate $\text{Cu}(\text{NO}_3)_2 + \text{HNO}_3$ is evaporated down and taken up with water, precipitating by NaOH the copper present, and determining it as oxide. This filtrate is to determine the copper oxide contained in the original substance.

Found copper oxide—

$$\begin{array}{l} \text{I. } 69.9949 \\ \text{II. } 71.6314 \end{array}$$

$\therefore$ Formula of the substance.

Found.

Oxygen	7.759
Copper	90.348
Metallic copper. . .	29.27
	61.078

Atomic Ratio.

Oxygen	7.759	} = $\text{Cu}_2 = \text{Cu}_2\text{O} + \text{Cu}.$
Copper	61.078	
Metallic copper ..	29.27	
	98.107	

$\therefore$ Found formula of substance $\text{Cu}_2\text{O} + \text{Cu}.$

W. R. Grove, in the same volume of the *Phil. Mag.*, p. 102, says:—

"It may be worth remarking that the quantities of nitrogen which enter into combination with the metals in these experiments are in proportion to their affinity for oxygen, and it may perhaps be considered an argument in addition to the many already advanced to prove that nitrogen is an oxide."

On Epidibromhydrine. — R. Lespieu. — Symmetric dibromhydrine was treated with phosphoric anhydride and distilled under a reduced pressure, when the product obtained separated into two principal parts, tribromhydrine, boiling at 219° , and $\text{C}_2\text{H}_4\text{Br}_2$, passing over at 91° and decomposing at 155° . — *Bull. Soc. Chim. de Paris*, vi. No. 6.

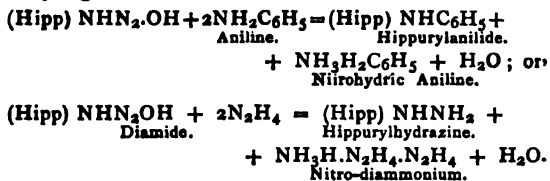
* "Inorganic Chemistry," vol. ii., "The Metals," p. 181, Section 139.
† "Dictionary," vol. ii., Con—Gyt, p. 67.

NITROHYDRIC ACID.*

By TH. CURTIUS.

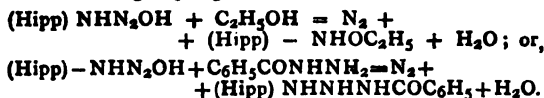
(Concluded from p. 300).

If nitro-hydrogen is eliminated an affinity is set free on the hippuryl, and is satisfied by the radicle of the attacking body, e.g.,—



A mol. of water is always split off at the same time.

If, on the other hand, nitrogen is eliminated in the reaction, there are formed bodies which are derived from hippuramide by the substitution of an atom of hydrogen of the amido group, e.g.,—



It will be seen that here also a mol. of water is split off.

Peculiar interest attaches to those derivatives which in the direction of the equation last given are formed by the action of primary acylhydrazines upon diazohippuramide. These bodies must be regarded as symmetric bis-acyl-derivatives of $\text{NH}_2\text{NH.NH}_2$, a triamide not yet known in the free state. The analysis, the origin, and the behaviour of these substances leaves no room for doubt that there exists in these bodies an open unramified chain of three imido-groups which are united with radicles on each hand. These substances possess so great a stability against alkalies or mineral acids that it has not been hitherto practicable to split off the acid radicles and to set the nitro-hydrogen, N_2H_5 , at liberty. It is scarcely to be doubted that further experiments will lead to the object and will be described in future.

Salts of Nitrohydric Acid. Nitrogen-Silver, N_3Ag .

Notwithstanding the remarkably explosive properties of this body (the silver in which has been already determined), an estimation of the nitrogen has been effected by combustion in a long column of copper oxide.

0.1076 grm. of this substance, when burnt with copper oxide, gave 26.0 c.c. of nitrogen at 6° and a pressure of 738.5 m.m., corresponding to 0.03077 grm. nitrogen at 0° and 760 m.m.

	Calculated for N_3Ag .	Found.
N/14	28.00	27.65 per cent.

The experiment succeeded once only; on repetitions, the tube, in spite of the most careful distribution of the material, was each time shattered.

Nitrogen-silver dissolves in ammonia, and crystallises on the evaporation of the ammoniacal liquid in needles, about a centimetre in length, nearly colourless, and fearfully explosive. The crystals explode sometimes on breaking. This compound is probably the silver salt and not a double ammonium compound, since the needles described are quite insoluble in water, and separate out only after the smell of ammonia has disappeared.

Nitrogen Mercurous Oxide. Nitrogen Calomel, N_3Hg .

This body is quite insoluble in water, like the silver salt.

If we wish to obtain nitro-hydrogen from the mother-liquors, they are best precipitated with mercurous nitrate,

aspirated dry, and thoroughly washed out with water. This salt has the advantage over the silver salt that it is more permanent, requires a higher temperature for ignition than the lead compound, the latter of which is, moreover, soluble in an excess of the precipitant. The precipitated mercurous salt form micro-crystalline anisotropic needles, which take a yellow colour on exposure to light, without undergoing any further change.

0.3866 grm. of the substance yielded, with lead chromate, 55.4 c.c. of nitrogen at 11.5° and 758.5 m.m. pressure, corresponding to 0.0669 grm. nitrogen at 0° and 760 m.m.

0.3057 grm. of the substance on suspension in water and treatment with H_2S , gave 0.2936 grm. mercury sulphide, = 0.2531 grm. mercury.

	Calculated for N_3Hg .	Found.
Hg	82.65	82.72 per cent.
N ₃	17.35	17.31 "
	100.00	100.03 "

Nitrogen calomel, if covered with ammonia water, forms a black insoluble compound.

Nitrogen Lead, N_6Pb .

Is precipitated from a solution of the sodium or ammonium salt on the addition of lead acetate; the precipitate is soluble in an excess of the precipitant. It is drained and frequently washed with water.

I. 0.1157 grm. substance yields with dilute sulphuric acid 0.1209 grm. PbSO_4 , representing 0.0826 grm. lead.

II. 0.1592 grm. of the substance evaporated down with dilute sulphuric acid gave 0.1665 grm. PbSO_4 , representing 0.1137 grm. lead.

	Calculated for PbN_6 .	Found.	
		I.	II.
Pb	71.13	71.33	71.40

Nitrogen lead is insoluble in cold water, and much more sparingly soluble in boiling water than lead chloride. According to superficial experiments, boiling water dissolves about $\frac{1}{4}$ grm. of the substance per litre.

ON CHEMISM IN LIVING PROTOPLASM.

By Prof. W. PREYER and G. WENDT (of Berlin).

(Continued from p. 288).

PROTOPLASM has a reticular structure. We may call it a highly complicated mixture or a kind of emulsion if we extend as far as possible the idea indicated by this word, and complete it by the determination that even in the free, non-nucleated, non-membranous protoplasm, which has not yet at any point reached a permanent differentiation, there is present a reticular or, as Bütschli names it, a comb-like (*wabig*, from *wabe*, a bee's comb) structure. Solid particles are suspended in the liquid, but even where every part seems physiologically equivalent to every other part, and not a trace of morphological individualisation is present, since separated portions are like whole, a mesh-work is still recognisable.

This architecture itself is mutable in one and the same object; in extended pseudopods it is indistinguishable, but visible in those half retracted, depending on the conditions of the surroundings in their often scarcely perceptible changes, as is proved by the observation (prolonged for hours) of living protozoa and the difference of the glandular cell protoplasm in action and in repose; and if the number of the chemical elements which can be isolated from any given protoplasm scarcely exceeds a dozen, the number of the combinations of these elements in such protoplasm is incalculable, because the compounds are themselves fluctuating.

* *Berichte der Deutsch. Chem. Gesell.*

The characteristic feature of protoplasm is its chemical and morphological variability, which, for every protoplasm adapted to given external conditions, still always leads us back to the same final products of metabolism. *e.g.*, carbon dioxide, and thus, notwithstanding the otherwise unlimited impressionability, implies for these processes of metabolism something in common.

But if innumerable substances mutable in the highest degree, especially albumens—some of which have been recognised in protoplasm—have shown for thousands of years not the slightest tendency to a chemical equilibrium or to a transition to stable combinations, as long as the protoplasm is alive, and therefore bid defiance to every chemical empiricism, if amidst endless variations a substance without parallel in its capacity for reactions, and yet completely devoid of characters in the opinion of theoretical chemistry, can be preserved through generations untold, we have a full proof that something other than ordinary chemical reactions has existed in it, in the living protoplasm down to the present day, and that there exists no prospect of ever explaining its peculiarity by such considerations.

In particular, the absence of chemical equilibrium proves the absence of mass action in the specific processes in question. In the living protoplasm in the cell that action of mass disappears, which in all chemical reactions ever tends to react chemical equilibrium. If it is objected that perhaps the time is wanting which is necessary for the termination of the reactions, and consequently for the attainment of chemical equilibrium and of stable compounds, which are not merely constituents of frame work or excretory matters, as a continued flux from cell to cell sweeps the newly formed substances too rapidly onward, it is clear that from cell to cell—indeed, in reproduction from organism to organism—more time is constantly given, and that in the enormous intervals since protoplasm came into existence a chemical equilibrium must long ago have been reached. But no rest ensues, as, for instance, in the formation of rocks. On the contrary, protoplasm in the course of the development of plants and animals has become increasingly sensitive and prone to decomposition.

For the chemical liability* of the protoplasm in the brain of vertebrate animals is greater than that of the infusoria, the chemism of the former involves more special conditions than that of the latter.

We must here always keep in mind that protoplasm is, in fact, immortal. Whatever external injurious agencies may in however short a time convert however many individuals into inorganic matter, *i.e.*, kill them, the root still remains. By the ovum, by the seminal filaments, even by the products of a sexual self-division (if such occurs without the antecedent contact of two protoplasmic structures), the physiological properties of the most ancient living being are inherited through all generations; but there is no heredity without a material substratum. The sole substratum of hereditary properties is protoplasm, which therefore must have preserved itself for millions of generations. And that there is no prospect of its entire annihilation is proved by the strict validity of the law of the "preservation of life."

In each single generation in each single function of each individual it is, again, the variability of protoplasm, its metabolism, its assimilation and dissimilation, which ever and ever, in an endless succession, effects with the same few organic elements the most highly complicated chemical synthesis and transformations. It sounds paradoxical, but we can scarcely express it otherwise:—

What is permanent in protoplasm is its variability. Its unparalleled liability can manifestly not be rendered intelligible by the theory of substitution by chemical affinity, by the theory of the action of masses, however many well-characterised compounds may have been obtained from protoplasm, *i.e.*, produced, doubtless, in part by the act of

preparation, and though even the occasional substitution of one element for another has been effected without an interruption of vital activity.

(To be continued).

TREATMENT OF ZIRCONS IN PREPARING PURE ZIRCONIUM CHLORIDES.

By F. P. VENABLE.

LINDEMANN (*Sitz. Ber. Kais. Akad. d. Wissenschaft*, vol. ii., 1885, translated in the *CHEMICAL NEWS*, vol. iii., 233 and 240) has published an account of the "Treatment and Qualitative Composition of Zircon." All previous methods of breaking up the zircon and purifying the zirconia have presented numerous difficulties and proved decidedly unsatisfactory.

Having occasion to prepare some of the compounds of zirconium in considerable quantity and of chemical purity, I adopted the methods of Lindemann. In the course of my work, I have found it advisable to modify the process in several respects, and I make this publication in order that my experience may be available, and perhaps serviceable, to others.

In the first place, I have found the mechanical preparation can be simplified. I have used North Carolina zircons, and have found it sufficient to pulverise them roughly in an iron mortar and then grind in an agate mortar until the powder passed through a 100-mesh sieve. The preliminary exposure during ten days to vapour of hydrofluoric acid and the grinding until the powder passed a silk sieve seemed both unnecessary. The fine powder was repeatedly boiled with strong hydrochloric acid and washed with water. 500 grms. treated in this way lost 17 grms., the hydrochloric acid thus dissolving 3.40 per cent of the whole. The fusions were made in nickel crucibles, which are very much cheaper and less attacked than the silver recommended by Lindemann. The loss comes chiefly in the cracking of the crucibles during the cooling after fusion. The crucibles used held a charge of 100 grms. zircon, 400 grms. sodium hydroxide, and 20 grms. sodium fluoride. This is one-half the amount of sodium fluoride recommended by Lindemann, but proved sufficient.

The sodium fluoride should be dried beforehand. The sodium hydroxide is first thoroughly melted and the fluoride then added. The mass should be brought to a fairly high temperature and then the zircon powder added. A rapid evolution of gas follows the introduction of the powder. The mass should be well stirred by means of a nickel stirrer—a narrow strip of sheet nickel fastened to a glass rod answers the purpose and keeps the hands beyond the reach of hot alkali occasionally thrown out. If the bubbles threaten to rise over the edge, temporary removal of the lamp secures their subsidence. The crucible should not be allowed to cool too far, however. Much seems to depend upon carrying through the reaction rapidly at a high temperature. I have at times doubled and even tripled the length of fusion at a lower temperature without securing the thorough breaking up of the zircons obtained at a high temperature. After the first violent boiling a quieter period follows. The end of the reaction is shown by a thickening of the mass and the rising of large bubbles here and there; also sometimes by a fine spitting or spray. In several instances where weights were kept the undissolved or unattacked portion of the zircon powder amounted to less than 0.5 per cent.

The melted mass was poured out upon pieces of sheet nickel for cooling. After solidifying enough to handle with tongs, it was broken off and plunged in a beaker of cold water. Water was also put in the crucible, after it had cooled, to dissolve off the portions adhering to the sides.

* "Liability," the antithesis to stability,—a useful term.

The water separates the sodium silicate from sodium zirconate, leaving the latter undissolved. The separation by means of water is far from perfect, some of the zirconate going into solution, though not enough usually to make it worth while to attempt to regain it. The sodium zirconate is dissolved in dilute hydrochloric acid and evaporated several times to dryness with fresh amounts of acid in order to drive off the hydrofluoric acid. There is a good deal of silica left with the undissolved portion. This is separated after evaporation to dryness. The dried mass is leached with dilute hydrochloric acid. There is difficulty sometimes in extracting all of the zirconium chloride in this way. Of course the solution contains large quantities of salt besides other substances. Zirconium hydroxide is precipitated from these by ammonium hydroxide, and then thoroughly washed in large jars by decantation. The crude zirconium hydroxide is next dissolved in strong hot hydrochloric acid, using as small an amount as possible. This solution is evaporated to dryness, and the crude zirconium chloride obtained placed in a large funnel and washed with a mixture of strong hydrochloric acid and four parts of alcohol. This mixture is poured upon the mass in the funnel and allowed slowly to drain through. Some zirconium chloride is dissolved, but can be recovered by evaporation. The mass in the funnel is left white, and fairly pure.

To complete the purification, this mass is taken and repeatedly crystallised from boiling hydrochloric acid, until the acid gives no test for iron, which seems the most persistent among the impurities. I have commonly found it well to repeat this crystallisation more than twenty times. The pure oxychloride is obtained in well-formed crystals of glistening whiteness. This method of crystallising from hydrochloric acid used by Linnemann is the only satisfactory one for purifying the zirconium chloride. I have tried the precipitation by hydrogen dioxide as recommended by Bailey, but the consumption of pure dioxide is very large, and a heavy source of expense, and the pentoxide or mixed oxides yielded is not nearly so convenient as the chloride for further working with.

The method described above is shorter than the tedious and expensive treatment with hydrochloric acid, alcohol, and ether. Judging from an attempt at carrying it out on a small scale, the amount of ether required in purifying the product from a kilo. of zircons would be very large indeed.

The modifications in the process have throughout the aim of cheapening and shortening Linnemann's process, and were successful in both directions, at least under the conditions under which I worked.

A qualitative analysis of the different products obtained while thus decomposing the zircon was made under my directions by Mr. John M. Morehead. It differed in several noteworthy particulars from that made by Linnemann.

In the first place, the hydrochloric acid used in the preliminary treatment of the zircon powder extracted a large part of the total tin present. Linnemann does not mention tin as occurring in this solution. No lithium was discovered in any of the solutions, nor any bismuth and zinc. The list of elements found by Mr. Morehead is, therefore, shorter than Linnemann's, who reports sixteen. The list found was sodium, potassium, magnesium, calcium, aluminium, iron, lead, tin, uranium, erbium, silicon, and zirconium. Undoubtedly, a large portion of these come from foreign matter mixed with the zircons and sifted into the cracks in the crystals so as not to admit of separation. A number of the rare elements were looked for without avail. No thorough spectroscopic examination was made, however.

Mr. Morehead also made several quantitative determinations of the iron, silicon, and zirconium, resulting as follows:—

Per cent Zirconium Dioxide	62.82	62.59	63.12	62.80
„ Silica	34.10	34.20	33.52	34.10
„ Ferric Oxide ..		3.29		

Or, taking the means,

ZrO ₂	= 62.83
SiO ₂	= 33.98
Fe ₂ O ₃	= 3.29
	100.10

It is not right to calculate the iron as all in the oxidised condition, as much of it comes from the iron mortar, and can be easily separated with a magnet.—*Journal of Analytical and Applied Chemistry*, v., No. 10.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

December 3rd, 1891.

Prof. A. CRUM-BROWN, F.R.S., President, in the Chair.

(Concluded from p. 307).

71. "Note on the Structure of Luminous Flames." By ARTHUR SMITHELLS, B.Sc.

The author gives a brief summary of the various views that have been held on this subject. With one or two exceptions, there has been general agreement since the time of Berzelius that an ordinary candle flame, or the flame of coal gas escaping from a circular hole, is divisible into four chief regions: (i.) the dark inner part; (ii.) the luminous part; (iii.) a small bright blue part at the base of the flame, thinning off rapidly as it extends upwards; (iv.) a dim, scarcely visible, faintly luminous mantle surrounding the whole flame.

The explanation which the author would give of these regions is as follows:—The gas or vaporised wax, on issuing from the orifice or wick, becomes mixed with air and burns. Whether or not the flame is luminous depends on the rate at which the combustible is supplied. If slowly supplied, sufficient air is admixed with the gas for non-luminous combustion. Thus a very small gas flame is non-luminous, and so also the flame of a candle, with the wick cropped close to the wax. It is conventionally said that coal gas burns with a luminous flame; it is just as true to say that it burns with a non-luminous flame. The small non-luminous flame of coal gas, or of a short wick candle, is seen to have the same structure as a Bunsen burner, viz., a bright blue inner cone, and a pale lilac cone superposed upon it. The author supposes that we have here the same chemical changes occurring as are dealt with in the previous paper, viz., that the first combustion in the inner cone is mainly to CO₂, H₂O, CO, and H₂, and the final one in the outer cone is mainly that of CO and H₂ to CO₂ and H₂O. This is made more probable by the fact that if the gas supply be increased, the luminous tip appears just at the point where it appears in the experiment with benzene, and that even after it is considerably developed the shape of the flame betrays the persistence of the inner cone. As the gas supply is further increased, the luminous area becomes increasingly great, the relics of the two original cones being very small.

The author's view is further enforced by the simple experiment of taking a flame about 5 c.m. high from a Bunsen burner with the air holes stopped, noting the blue region at the base of the flame and the dim mantle outside it and then gradually turning on the air. The gradual transition shows unmistakably that the blue part and the mantle are the "rudiments" of the two cones of a Bunsen flame.

With regard to the luminous part, everything goes to

show that it is mainly a region where hydrocarbons are decomposed by the heat of the outer parts of the flame. The precise nature of the change is being studied by the author.

The dark inner cone contains mainly unburned gas, mixed with some products of combustion from surrounding regions.

A commonly held view that the mantle of a luminous flame is due to heated air and products of combustion is inconsistent with the above explanation, and also with the fact that in recent experiments it has been found impossible to render air luminous at the highest attainable temperatures.

The view that carbon is separated in a flame owing to the preferential combination of oxygen with hydrogen, is opposed, the author thinks, to all experimental evidence, which he is of opinion goes to show that if the oxygen supply be limited carbon will burn before hydrogen.

The author would describe a luminous flame as follows:—

(i.) An outer sheath or mantle, with (ii.) an inner bright blue portion visible at the base of the flame. These two parts correspond respectively to the outer and inner flame cones of a Bunsen flame, and mark the region where the coal gas or candle gas is burning with a large quantity of air.

(iii.) The yellow luminous part marking the region where the heat of the parts (i.) and (ii.) is decomposing hydrocarbons, setting free carbon, which rapidly glows and burns.

(iv.) The dark inner region, consisting of unburned gas, mixed with products of combustion of surrounding parts.

Novelty is not claimed for this description, but the author considers that the experiments described in the preceding paper put the matter in a somewhat new light.

72. "The Existence of Hyoscyamine in Lettuce." By T. S. DYMOND.

Lettuce has been used in medicine from early times as a sedative, but the active constituent has never been with certainty determined. The author's attention was drawn a few months ago to the mydriatic action of an extract of lettuce used in medicine. It had been prepared from the flowering plant of common lettuce according to the directions of the "British Pharmacopœia. An examination showed that the mydriatic action was due to an alkaloid. Commercial specimens of the extract of wild lettuce and of the variety of the edible plant known as cos lettuce, obtained from three different sources, together with a specimen of the dried flowering plant of wild lettuce, were all found to contain this alkaloid.

The alkaloid was most easily isolated by mixing the commercial extract with water acidified with acetic acid, adding alcohol till precipitation of nearly all the constituents of the extract occurred, filtering, evaporating the filtrate to a low bulk, filtering again, washing the filtrate with ether till free from fat, then rendering it alkaline, and extracting the alkaloid with ether. The impure alkaloid thus obtained was purified by conversion into the oxalate, and the precipitation of this salt by ether from its alcoholic solution. On recovering the alkaloid and crystallising it from chloroform, it was obtained in silky needles having approximately the same melting point and other properties as hyoscyamine, the poisonous mydriatic alkaloid existing in belladonna, henbane, and other plants belonging to the natural order *Solanaceæ*.

The identity of the alkaloid with hyoscyamine was confirmed by conversion into the aurichloride, which melted at 159.75, the melting point given by Ladenburg for hyoscyamine aurichloride being 159. The determination of the gold and the alkaloid in the compound afforded results corresponding with the formula of hyoscyamine aurichloride, $C_{17}H_{23}NO_3 \cdot HAuCl_4$.

The amount of hyoscyamine in the extract of common lettuce does not exceed 0.02 per cent, while in the flowering plant itself it cannot be more than 0.001 per

cent. It appears that this is the first occasion on which hyoscyamine or any other alkaloid belonging to that mydriatic group has been found in a plant not a member of the natural order *Solanaceæ*, lettuce belonging to the natural order *Compositæ*.

DISCUSSION.

Professor DUNSTAN pointed out that it had been known from the time of the Greeks that lettuce had a soporific action, and as Ladenburg and others had shown hyoscyamine to be a soporific, it was now possible for the first time to explain an ancient Grecian practice.

73. "Cryptopine." By D. RAINY BROWN and W. H. PERKIN, jun., Ph.D., F.R.S.

The authors have commenced an investigation on the rare alkaloid cryptopine, which occurs in small quantity in opium, and which was first isolated by J. and H. Smith (*Fahresbericht*, 1867, 523), and subsequently analysed by Hesse (*Annalen*, Suppl., viii., 209).

Analyses of the base and of several of its salts led Hesse to assign to cryptopine the formula $C_{21}H_{23}NO_5$. The authors have prepared and analysed several samples which had been purified by conversion into the oxalate and subsequent re-crystallisation from isobutyl alcohol. The mean result of five analyses was—

	Per cent.	Theory for $C_{21}H_{23}NO_5$. Per cent.
C	68.23	68.29
H	6.34	6.23
N	4.15	3.79

The oxalate, after repeated recrystallisation from water, was obtained in the form of beautiful glistening prisms, which, on analysis, gave the following numbers as the mean of four experiments:—

	Per cent.	Theory for $C_{21}H_{23}NO_5 \cdot C_2H_2O_4$. Per cent.
C	59.82	60.13
H	5.55	5.44
N	3.31	3.05

These analyses confirm Hesse's results, and show that cryptopine has the formula $C_{21}H_{23}NO_5$.

On oxidation with potassium permanganate, cryptopine yields among other products a crystalline acid, $C_{10}H_{10}O_6$, m. p. 179–180°, which proves to be metahemipinic acid, $C_6H_2(CH_3O)_2(COOH)_2$ [1 : 2 : 4 : 5], the acid which Goldschmidt obtained from papaverine; this result is interesting in view of the fact that metahemipinic acid, up to the present time, has only been obtained from papaverine.

The identity of the acid obtained from cryptopine with that from papaverine was proved by the fact that both yield an anhydride, $C_{10}H_8O_5$, m. p. 175°, and an ethylimide, $C_{12}H_{13}NO_4$, melting at 226°.

Cryptopine contains only two methoxy-groups, as shown by its behaviour when treated with hydrogen iodide, these two groups being situated in that part of the molecule which is converted into metahemipinic acid on oxidation.

74. "The Action of Sodium on Ethereal Salts. Part III. Benzylic Orthotoluate." By W. R. HODGKINSON.

The behaviour of the different ethylic toluylates towards sodium was briefly referred to in these *Proceedings* in 1886 (p. 188).

In all cases their behaviour is different to that of the ethylic salts of phenylacetic acid. No trace of any substituted acetic or benzenoid fatty acid could be found, and the action differs moreover in that no ring condensation appears to take place, as is the case with ethylic phenylacetate, which affords "triphenylphloroglucol."

In the case of the benzylic salt of orthotoluic acid, it was thought that either the CH_2 might act in a similar manner to the CH_2 in phenylacetic acid, or that two molecules would condense, forming dimethylantranthraquinone and benzylic alcohol.

Benzylic orthotoluate, $C_6H_4Me \cdot CO_2 \cdot CH_2Ph$, which

does not appear to have been previously formed, is a liquid of very pale-yellow colour which boils without the least decomposition at 315° (thermometer in vapour). Rel. den. at 17° 1.12.

As mentioned in connection with triphenylphloroglucol, the products of the action of sodium on these ethereal salts differ considerably according to the conditions of the experiment. On adding the sodium to the oil previously heated to 200° it dissolved, and the temperature rose to 250° , when an oil distilled over. This, on fractional distillation, separated into toluene and benzyl alcohol for the most part, with a smaller quantum of the original ethereal salt. The sodium salt in the retort dissolved in water, and gave on treatment in the usual manner an oil and an acid. This acid is pure *o*-toluic acid. The oil was found to consist of unchanged benzylic orthotoluic acid and a substance boiling at 350° (nitrogen thermometer in vapour) 360° .

This substance remained liquid at -10° and could scarcely be a derivative of anthraquinone. Analysis shows it to have the composition $C_{22}H_{20}O_2$, which is that of a substance of the formula $C_6H_4Me.CO_2.CHPh$ (CH_3Ph).

The quantity at present disposal has allowed only of hydrolysis with potassium hydroxide, from which it appears that only *o*-toluic acid is formed, and an oil which boils at about 250 — 280° . The matter is still under investigation.

75. "The Gas-Volumeter and Gravisvolumeter." By G. LUNGE.

In this note the author comments on Professor Japp's reply to his criticisms (*Ber.*, xxiv., 1856).

76. "The Action of Sulphuric Acid on the Bromides of Hydrogen, Potassium, and Sodium." By F. T. ADDYMAN, B.Sc.

The author has sought to determine the extent to which hydrogen bromide is oxidised by sulphuric acid under varying conditions of mass and dilution.

He first describes experiments in which sulphuric acid ($d=1.84$) was allowed to act on potassium bromide, from which he infers that the amount of decomposition which the hydrogen bromide undergoes is very nearly proportional to the amount of sulphuric acid used; but it is subsequently admitted that the extent to which the hydrogen bromide and acid come into contact greatly affects the result, so that a higher percentage would be decomposed in a deep than in a shallow vessel.

In the second section of the paper, a method of preparing a solution of hydrogen bromide is described, very similar to that of Feit and Kubierschky (*C. S. Abstracts*, 1891, 1320). An account is then given of observations on the amount of change produced by sulphuric acid in solutions of hydrogen, potassium, and sodium bromides. But mere traces of bromine are liberated in solutions containing not more than about 30 per cent of sulphuric acid; and the percentage of hydrogen bromide decomposed is but small, even when as much as about 70 per cent of sulphuric acid is present.

77. "The Iodometric Estimation of Chlorates." By G. MCGOWAN, Ph.D.

Attention is called to Finkener's statement, that when Bunsen's method is applied to chlorates, less than the theoretical amount of chlorine is evolved. Experiments are then described, made in accordance with the method, and with the apparatus of which an account is given at pp. 530—536 of this year's volume of the Society's *Transactions*, which corroborate the results of de Koninck and Nihoul, and prove the accuracy of the Bunsen method; Finkener's error doubtless arose from a slight loss of chlorine. The author emphasizes the importance of carrying out all such determinations in an apparatus in which the chlorine does not come into contact with india-rubber.

NOTICES OF BOOKS.

Quantitative Chemical Analysis. Adapted for Use in the Laboratories of Colleges and Schools. By F. CLOWES, D.Sc., Professor of Chemistry in the University College, Nottingham, and J. BERNARD COLEMAN, Associate of the Royal College of Science, Dublin; Senior Demonstrator of Chemistry in the University College, Nottingham. London: J. and A. Churchill. Small 8vo., pp. 409.

A TRULY admirable book! Every chemist who gives it a fair examination will be convinced that it could never have been written by compilers, who too often carefully appropriate the "gange" of the works which they prey upon, neglecting the gold. Even less could it be produced by careless, incompetent workers, heedless or ignorant of the niceties which are required for accurate work. The authors, following in this respect the sound example of Rose and Fresenius, have, as they tell us in the preface, "kept their work within moderate dimensions, firstly by omitting unnecessary theoretical matter," and secondly, by "inserting only typical, useful, and well-accredited methods."

A useful and commendable feature is the bibliography placed at the beginning of the book for the benefit of students who wish for more detailed instruction on any particular subject.

The table of contents gives in parallel columns the paragraphs and the pages where any particular subject may be found.

The first part of the book supplies general instructions, directions for weighing—carefully written—the determination of specific gravities, melting- and boiling-points, mechanical comminution, drying, solution, precipitation and general instruction in manipulation.

Part II. gives directions for simple gravimetric determination. Part III. treats of volumetry. Part IV. is devoted to general analysis, including, of course, separations. Its subdivisions are technical analysis, water analysis, and food analysis, along with which comes the quantitative examination of tannin and soaps; and ultimate organic analysis. Part V. is taken up with gas analysis, a department which in many treatises is either very superficially treated or altogether overlooked.

An appendix supplies the preparation of gases for analytical processes, results of the analysis of typical specimens, tables of useful constants and memoranda. Lastly comes a list of the apparatus and the chemicals required for the processes prescribed in the text.

We feel it our agreeable duty to give this work our warm recommendation both for what it contains and for what it ignores.

A Graduated Course of Natural Science, Experimental and Theoretical. For Schools and Colleges. Part II. Second and Third Year's Course. For the Intermediate Classes of Colleges and Technical Schools. By B. LOEWY, F.R.A.S., Examiner in Experimental Physics to the College of Preceptors, London. With sixty diagrams. London and New York: Macmillan and Co. Small 8vo., pp. 257.

THIS is a treatise on what we formerly called "natural philosophy." The author is perfectly justified in holding that such a general or introductory course should precede more special studies. We may, perhaps, take exception to the term "natural science" in the title, and submit that physical science would have been a happier expression. The words "natural" and "physical" are, of course, unmistakably synonymous, but of late years custom has more or less allotted the term "physical science" to the inorganic disciplines, physics, chemistry, astronomy, &c., confining the phrase "natural science" to biology in all its branches.

We find in this book nothing questionable or excep-

tional except it may be the contention that sound is a form of energy. On this question we feel exceedingly doubtful. It is certainly not reciprocally convertible into light or heat. Nor can we calculate its mechanical equivalent. Nor is it known to fulfil any natural function save as communicating ideas or emotions from one sentient being to another. Turning aside, however, from this doubtless unprofitable question, we may remark that this work is characterised by great clearness of exposition. The experiments are well selected and easy of performance, and the illustrations are well drawn and useful.

Elementary Inorganic Chemistry. Theoretical and Practical. With a Course of Chemical Analysis and a Series of Examples in Chemical Arithmetic. By A. HUMBOLDT SEXTON, F.R.S.E., F.I.C., F.C.S. New Edition. London: Blackie and Son, Lim. Fcap. 8vo., pp. 320.

THIS book is typically examinational. The author refers to the great number of students "presenting themselves for examination" under the Science and Art Department as his reason for keeping the requirements of the Syllabus of the Department before him in preparing his book. He, however, "has not hesitated to go beyond the Syllabus where he has felt it advisable." In his arrangement of the elements he ignores the periodic classification, and in his account of the non-metallic bodies silicon and its compounds are omitted! Among the metals, gold, platinum, nickel, cobalt, antimony, arsenic, tin, zinc, not to speak of the rarer metals, are left out.

We find a series of questions and ten pages of examination papers set by the Department.

An interesting note at the conclusion of the preface is that Part V.—the elementary course of qualitative analysis—"has been re-cast to meet the alterations in the Syllabus of the Science and Art Department." Thus we see that teachers, if they wish their pupils to "pass," have to teach, not the Science, but such portions of the Science as the Department takes for the time being into favour. The examiner in this country dictates to the teacher.

We are often encountered by the cavil that without examinations it would not be possible to separate the wheat from the chaff. We maintain that the separation takes place more easily and thoroughly in real life than at any examination. Everyone knows the splendid position which Germany takes in Science. Yet she has no works written for the use of students preparing for this or the other examination. Our system, in fact, creates the chaff which has to be winnowed out. We would suppress all intermediate examinations and for the final test demand the production of original work in some science. The London University now demands research, but merely in addition to, not in lieu of, "passing."

The Alkali Makers' Handbook. Tables and Analytical Methods for Manufacturers of Sulphuric Acid, Nitric Acid, Soda, Potash, and Ammonia. By GEORGE LUNGE, Ph.D., Professor of Technical Chemistry, Zurich, and FERDINAND HURTER, Ph.D., Consulting Chemist to the United Alkali Company, Limited. Second Edition, enlarged and thoroughly revised. London: Whittaker and Co., and G. Bell and Sons. Small 8vo., pp. 184.

THIS work, which belongs to the "Specialists' Series," issued by the publishers above named, must be pronounced exceedingly useful.

The first edition appeared as the Alkali Makers' Pocket Book, but an increase of size has indicated its present title. The fundamental purpose of the work, entertained by a number of German alkali makers and technical chemists, was to furnish, for each raw material, and for

each product intermediate, fixed, or secondary, some one analytical process.

This one process should in each case be the best known, understanding by "best" the most convenient and expeditious as well as the most accurate. This agreement was necessitated by the number and the magnitude of commercial transactions in connection with the alkali manufacture. Hence it was of great importance to have what we may call authorised methods by which each party to a contract or to a lawsuit should be prepared to stand or fall. These standard methods have been, we are told, accepted to a very great degree by German alkali makers, by their customers, and by commercial analysts. The work has been issued also in the English language, in the hope that its leading principle may be accepted in this country also. This seems to us a most laudable undertaking, as calculated to prevent unifying disputes. It has been necessary to recalculate a number of tables here given in accordance with British weights and measures. Had we adopted the principle—we do not say the nomenclature—of the metric system, this labour might have been saved.

We first find here a table of the atomic and equivalent weights, symbols, and valencies of the elements, round numbers being made use of. The authors have thought fit to give tungsten the name "Wolframium," which, as they cannot help knowing, is not used in the English language. Of more importance is the fact that, following the lead of the "Potash Convention," they give for platinum the obsolete atomic weight 197.18. This is the more remarkable as Continental authorities have always taken up their parable against the British alkali trade for still giving to sodium the atomic weight 22.

Another table gives the more accurate weights of the elements according to Professor Ostwald.

The table of factors for calculating grammatical analyses is in principle like that met with in Rose's "Quantitative Analysis," and will be valuable and trustworthy except where the erroneous atomic weight of platinum interferes.

After a number of other tables important to alkali manufacturers, chemists, and managers, we come to the special part including the analytical process recommended. Due attention is here paid to gas analysis, without which it is no longer practicable to conduct alkali works safely and successfully. It is remarkable that whilst the quantity of sulphurous acid escaping into the atmosphere from any other source is now strictly defined, that generated by the consumption of coal or coke is placed under no restrictions. What penalties would be incurred by any chemical manufacturer who should keep up in or around his works an atmosphere like that found in certain parts of the Underground Railway?

We feel certain that this "Handbook" will find numerous and appreciative readers among all persons connected with the alkali trade.

A Handbook of Industrial Organic Chemistry, adapted for the use of Manufacturers, Chemists, and all interested in the Utilisation of Organic Materials in the Industrial Arts. By S. P. SADTLER, Ph.D., F.C.S. London and Berlin, Member of the Society of Chemical Industry, &c. Philadelphia: J. B. Lippincott and Co. 8vo., pp. 519.

THE author of this treatise states that in the English language we have in general chemical technology "only the now antiquated technology of Wagner and Payen." He qualifies this assertion, however, by admitting that he refers "only to general works on chemical technology of moderate size." Dr. Sadtler must be aware that to compress a general view of chemical technology within a single volume of moderate size is becoming more and more difficult, if the accounts of the various processes are to enter sufficiently into useful details. In works dealing with single departments of the chemical arts our litera-

ture is fairly rich. To many of these works, indeed, he refers in the bibliographical notes placed at the end of each subject. Of course the author economises space by confining himself in this work to the organic chemical industries. This distinction, however, is difficult to carry out. Thus we find here included the manufacture of inorganic mordants, brief sections on the purification of water for industrial uses, an account of dynamite and some of its kindred bodies, &c. On the other hand, matches, phosphorus, and chemical manures are omitted, though a large portion of their ingredients must be pronounced organic. The oxalic, tartaric, citric, and malic acids do not seem to have fallen within the author's plan, no more than quinine, morphine, &c. We might naturally have expected that of quinine, which is now obtained on so extensive a scale. These omissions are the more remarkable as the author describes himself as chemical editor of the United States Dispensatory, Professor of Chemistry in the Philadelphia College of Pharmacy.

The bibliographical sections we have already pronounced useful, but their value would have been increased if the name of the publisher of each work had been given. To say that a book is published in London, Paris, or Leipzig, as the case may be, is often insufficient.

As regards the subject matter of the work, its general character is correctness. Still greater details would in many cases have been highly desirable. In some cases the arrangement adopted is, at least, peculiar. Thus we find nitroglycerin and dynamite under the head "Fats and Fatty Oils," whilst their near neighbour gun-cotton is to be sought under "Vegetable Textile Fibres." Printing inks come under "Essential Oils and Resins," and writing inks apparently nowhere.

Great care has evidently been expended on getting up the statistical appendices.

A Practical Introduction to the Elements of Chemistry.
By W. MARSHALL WATTS, D.Sc. (Lond.), B.Sc. (Vict.), F.I.C. London: Nisbet and Co. Small 8vo., pp. 128.

THIS little work belongs to a series entitled "Nisbet's Elementary Science Manuals," prepared, it is stated, for the "Oxford and Cambridge Local Examinations," though they are also intended for "School and Family Use."

In the preface, the author, or else the general editor, Rev. J. H. Whitehead, M.A., whose functions do not very clearly appear, informs us that the "plan of the present work differs somewhat from that usual in small books of a similar title." It is "experimental from the very beginning." So numerous, however, are the elementary manuals of chemistry used, or at least published, in this country, and so slight are the shades of difference between them, that we cannot venture to say in how far the author's claim can be substantiated. Our own opinion is that there is here little, if anything, which has not already been said clearly and repeatedly.

CORRESPONDENCE.

NEW METHYLATED SPIRIT.

To the Editor of the Chemical News.

SIR,—I have read the note on "new methylated spirit" in the CHEMICAL NEWS (vol. lxiv., p. 310), and at the council meeting of the Royal Microscopical Society on Wednesday last I had some conversation on the subject of the new regulations and gave notice of my intention to bring it before the next meeting.

By the new order histologists are deprived of their most valuable reagent. Alcohol in histology, like sulphuric acid

in chemistry, is the key to most of the work, and a heavy duty on either would bring work to a standstill.

Among the societies whose members are affected besides the Royal Microscopical, are the Chemical, Photographic, Linnean, Zoological, &c. Hospitals, large museums, and medical schools are able to obtain quantities of 5 gallons and upwards of the old kind of spirit; but small laboratories and the whole race of amateurs must either leave off work or pay the duty of ten shillings and sixpence per gallon. Truly "endowment of research" with a vengeance!

We considered at the Royal Microscopical Society that several of the other societies might take united action in the matter, and bring a little pressure to bear upon the Inland Revenue authorities, who, we may charitably suppose, are quite ignorant of the mischief they are doing.

I should be glad if you could in any way aid me in this matter.—I am, &c.,

W. T. SUFFOLK.

December 19th, 1891.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxiii., No. 23, December 7.

Reply to a Paper by M. Besson on Boron Phosphide.—Henri Moissan.—A question of priority.

The Works of Scheele.—M. Nordenskiöld, in a letter addressed to M. Berthelot, announces that he has undertaken the publication of the hitherto unpublished letters and memoirs of Scheele. The letters are composed in a clear and concise style. They contain exclusively accounts of chemical experiments, novel, and generally important. There scarcely ever occurs in them a useless phrase which might be suppressed or modified.

Report on the De-plastering of Wines.—The Syndical Chamber of the wine and spirit trade of Paris and the Seine apply for the opinion of the Academy on the use of the salts of strontium for de-plastering wines.

Vapour Tensions of Solutions of Cobalt Chloride.—Georges Charpy.—Referring to Etard's recent paper on the solubility of cobalt chloride, the author has observed facts of the same order whilst studying the vapour tensions of the solutions of cobalt chloride. The facts, like those observed by Etard, lead us to admit the existence of two stable conditions of cobalt chloride. This change of condition may be ascribed either to a variation in the state of hydration of the salt, or to a change in its molecular aggregation.

Action of Sodammonium and Potassammonium upon Certain Metals.—M. Joannis.—Sodammonium and potassammonium are decomposed by several metals, especially by mercury, lead, and antimony. Sodammonium is without action upon aluminium, silver, lead, and copper. The author examines in detail the action of these two compounds upon mercury and lead. With an excess of lead he obtains a compound, $Pb_4Na_2NH_3$, of deep indigo blue colour, which dissolves in ammonia with a bottle-green colour.

Calculation of the Temperature of Ebullition of the Isomeric Ethers of the Fatty Acids.—G. Hinrichs.—This paper cannot be reproduced without the accompanying diagram.

Thermic Data on Active Malic Acid and the Potassium and Sodium Malates.—G. Massol.—This paper does not admit of useful abridgment.

The Rotatory Power of Silk.—Leo Vignon.—Silk ranks, as regards its chemical constitution, among the albumenoid substances. If treated in heat with dilute sulphuric acid it yields among its decomposition products leucine and tyrosine. The solutions of the two principal portions of the silk of *Bombyx mori* (the "gum" in soda and the fibroine in hydrochloric acid) both exert a considerable action upon polarised light. Both are strongly lævo-rotatory, their rotatory power being close upon -40° .

Ammonia in Atmospheric Waters.—Albert Lévy.—The author questions the values given by MM. Marciano and Muntz in their recent memoir. He notes that in England Messrs. Lawes and Gilbert obtained in 1856 1.43 m.grm.—a figure very close upon that obtained in Caracas. His own analyses of the rains falling at Mont-souris during the last sixteen years (a yearly mean of 150 showers), give an average weight of 2.2 m.grms. of ammonia per litre of water, a figure higher than that obtained at Caracas.

Zeitschrift für Analytische Chemie.
Vol. xxx., Part 4.

Studies on the Ripening of Cherries, on the Fermentation Products of Cherry and Currant Juice, and on the Colouring-Matter of the Red and the Black Currant.—W. Klein.—This memoir, which runs to 25 pp., and includes seven tables and a plate showing the absorption-spectra of the products, does not admit either of useful abstraction or insertion in full.

Antimony Pentasulphide.—Th. Wilm.—According to the author the compound met with in commerce as "golden sulphuret" is not always an antimony pentasulphide (Sb_2S_5), but a mixture of antimony tersulphide with free sulphur, or of the penta- and tersulphides with sulphur. He shows that the determination of the sulphur capable of extraction by means of carbon disulphide does not lead to satisfactory results. For the determination of total sulphur he recommends oxidation with fuming nitric acid in a sealed tube. A determination in an Erlenmeyer flask did not give constant results. He heats for 2—3 hours not above 130° , when no explosion takes place. On opening the tube a little water is added, when the contents turn green or bluish-green, and a quantity of gas escapes. When this reaction is over, the glass is nearly filled with concentrated hydrochloric acid, and heated in the water-bath until the white powder is completely dissolved. The whole is then rinsed into a porcelain capsule, evaporated down as far as practicable on the water-bath, covers the moist residue with a little concentrated hydrochloric acid, applies heat and adds a solution of tartaric acid. The boiling solution is precipitated with barium chloride, and the barium sulphate filtered off after standing for 10—12 hours.

Universal Gas-Holder.—Dr. Eichhorn.—This apparatus, the construction of which cannot be described intelligibly without the accompanying figure, serves at once as a gas-holder, a blast, a compression-pump, and a rarefying apparatus.

Glass Vessels for Scientific Purposes.—Leybolds (Cologne).—These vessels, some of which are here figured, are cells with flat sides made of uniform thickness and free from bubbles or waviness. They are recommended for various chemical, physical, bacteriological, &c., uses.

Separation of Barium and Calcium.—R. Fresenius.—The concluding portion of a memoir which will be presently reproduced.

The Question of Introducing the True Litre, or retaining that of Mohr in Volumetric Analysis.—W. Fresenius.—The author decides in favour of retaining the litre of Mohr, i.e., the volume of a kilo. of water at 175° , as weighed in the air with brass weights.

Spectra of the Elements of Mendeleeff's Second Group.—H. Kayser and C. Runge (*Annalen der Physik*).—No details are given.

Colorimetric Apparatus and Methods, and Quantitative Spectrum Analysis.—G. Krüss and H. Krüss.—A work published by L. Voss, Hamburg. No particulars are here given.

A Spectro-Colorimeter.—D'Arsonval (*Seances Soc. Franc. de Phys.*).—Already inserted.

A Graphic Table for finding the Correction of the Readings of the Barometer.—(Necessary on account of the reduction to 0° for the expansion of the mercury).—R. Mehmke (*Annalen der Physik*).—No particulars are here given.

Influence of Pressure upon the Electroconductivity of Liquids.—C. Barus (*Silliman's Journal*).—No particulars.

Distinctions between α - and β -Naphthol.—N. Yvon.—To 10 c.c. of a saturated aqueous solution of naphthol there are added: (1) Alcohol 2 c.c., nitric acid 2 c.c., mercury nitrates 10 drops; (2) alcohol 2 c.c., potassium nitrate (saturated solution) 3 drops, sulphuric acid 10 drops. These reagents produce colour reactions as follows. In α -naphthol:—Reagent 1, the yellow colour of the mixture is not changed on boiling; chloroform is coloured yellow and ether yellowish-green; gun-cotton is dyed yellow, sulphurous acid renders the mixture immediately turbid with separation of a red precipitate. Reagent 2, on the other hand, turns the reddish-brown colour of the mixture to a brown on boiling; chloroform is coloured greenish-brown, and ether a yellowish-green; gun-cotton is dyed a dirty yellow. Sulphurous acid turns the mixture a dirty green without precipitation. With β -naphthol and No. 1 reagent the intense orange yellow colour passes at once into an orange red and is not altered by boiling; gun-cotton is dyed a rose red; the mixture colours chloroform a ruby red, and ether a yellow. Sulphurous acid gives the mixture a rose colour, which disappears very gradually, whilst a yellow or black precipitate is formed. With reagent No. 2 there is produced an intense violet red not changed by boiling; gun-cotton is dyed a vinous red, chloroform is coloured a greenish yellow and ether a yellow; the red colour is at once destroyed by sulphurous acid, but without precipitation. By means of these reactions the author succeeded in detecting β -naphthol in urine, but not α naphthol.

Detection of the Amines of the Aromatic Series.—Ch. Laub (*Comptes Rendus*).—Already inserted.

Elementary Analysis of Volatile Liquids.—E. Reichardt (*Archiv. der Pharm.*).—Very volatile liquids are weighed off in a small glass tube which fits into the platinum boat to be used. The glass tube is sealed below, rounded off above, and may be closed with a cork. It is half filled with copper oxide previously ignited, and fixed in a suitable vessel in a perpendicular position for weighing. The liquid to be analysed is now added, the tube is weighed again and filled up with copper oxide. When closed by means of a cork the liquid may thus be preserved. When the combustion is undertaken the open tube is placed in the platinum boat, the bottom of which is covered with a little copper oxide to prevent adhesion. The boat is pushed into the combustion-tube, and the combustion is then carried out in the usual manner in a current of oxygen. It is indifferent whether the open end of the little glass tube is turned towards the absorption apparatus or the closed end of the combustion tube. Experiments with volatile oils and with ethylic alcohol gave satisfactory results. In the elementary analysis of sparingly volatile liquids, we may, according to the author, place the liquid in question, drop by drop, upon the bottom of the platinum boat, previously ignited, and covered with copper oxide, and push it rapidly into the combustion-tube. An attraction of moisture is not to be apprehended.

Electro-conductivity of Boric Acid in presence of Mannite, Dulcitol, and Polyvalent Alcohols.—G. Magnanini (*Rendicont della R. Acc. dei Lincei*).—The molecular conductivity of boric acid, which is *per se* smaller than 6 units, rises in presence of mannite to 300, 500, and upwards, according to the quantity of mannite. The molecular conductivity of boric acid in presence of mannite decreases with dilution.

Ascent of Solutions in Capillary Tubes, and the Law of these Phenomena.—M. Goldstein (*Zeit. Phys. Chemie*).—The author proposes the law—

$$\frac{H-h}{H.M} i = C,$$

where H is the height of ascent of the water, h that of the solution, M the molecular weight of the dissolved substance, i the Van't Hoff co-efficient, and C a constant which varies with the percentage of the dissolved substance.

The Use of the Pendulum as a Balance.—K. Fuchs (*Zeit. Phys. Chemie*).—Already inserted.

Determination of Specific Gravities.—L. Amat.—From the *Bulletin de la Soc. Chimique de Paris*.

Reading Hydrometers.—C. Margoni and Grattorola (*Rendi. Acc. dei Lincei*).—In case of opaque liquids the authors apply a ring of platinum wire to the sides of the vessel in which the stem of the hydrometer goes up and down.

Apparatus for Determining the Specific Gravity of Solids.—W. Brown.—From *Industries and Chemiker Zeitung*.

A Thermo-Electric Battery.—Gülcher (*Elektrotech. Anzeiger*).—The elements are hollow bodies or combinations of such with massive rods. A battery of fifty elements is about equal to two Bunsen elements. The hourly working cost is 3–3½ pfennige.

Analysis of Sodium Aluminate.—G. Lunge (*Zeit. Angew. Chemie*).—Already inserted.

Separation and Determination of Antimony.—J. Thiee (*Liebig's Annalen*).—This paper will be inserted in *extenso*.

Separation and Determination of Tellurium.—E. Donath (*Zeit. Angew. Chemie*).—Already inserted.

New Method for Examining Ferrocyanides for Determining the Contents of Prussiate Melts, and of the Ferrocyanides in Spent Masses from Gas-Purifiers.—R. Zaloziecki (*Zeit. Angew. Chemie*).—Already inserted.

MISCELLANEOUS.

The Late Prof. Stas.—It is generally known that the papers of Stas are characterised not by their bulk and number, but by their sterling value. As far back as 1838 he published his researches on phloridzine. In 1849 there appeared his memoir on the true atomic weight of carbon. Two years later he communicated a valuable method for detecting alkaloids in poisoning cases. It will be remembered that he was the trusted and trustworthy adviser of the Belgian authorities on all questions of a chemical nature. In 1860 he began the publication of his *magnum opus*,—the inquiry into the reciprocal relations of the atomic weights. This long and laborious inquiry was undertaken with a view of deciding on the validity of Prout's law. As we need scarcely remind the reader, the conclusion was negative. The atomic weights examined were not found to be exact multiples by whole numbers, either of 1,—the atomic weight of hydrogen,—or of 0.5 or 0.25. On this point there arose some controversy with Prof. Marignac. But whatever may be the meaning of the remarkable fact

that the atomic weights of many elements approximate very closely to the values which Prout's law would require, the determinations of Stas have not been successfully challenged either in principle or in detail. His memoirs will be found in the earlier numbers of the CHEMICAL NEWS.

Diaries for 1892. — Messrs. Cassell and Co., the publishers of Letts's Diaries, have as usual sent us a selection for the approaching year. These are too well known and have secured too firm a hold upon the public for any detailed description to be necessary. The most generally useful to men of business will be the Rough and Commercial series, foolscap size, with a week to an opening. Those who require a smaller sized diary for the office table cannot do better than choose the Office edition, post octavo size. This contains a day on a page, and in addition gives information on postal, commercial, legal, and diplomatic matters, which are often required. However, in the list of ambassadors abroad we notice that our representative in France is still given as the Right Honourable the Earl of Lytton, whilst Mr. W. H. Smith is mentioned as the First Lord of the Treasury, and Mr. Balfour the Chief Secretary for Ireland. The Pocket editions with a week on a page are similar to the above, but smaller. The diary of most use to medical men will perhaps be the Medical Diary, which contains notes, information, and headings specially required in practice. It would be of great value to all our readers if Messrs. Cassell could see their way to bring out a similar diary for the use of men of science and chemists in general. Besides these there are a series of pocket books for ladies and gentlemen, which contain memoranda likely to be of special interest.

MEETINGS FOR THE WEEK.

TUESDAY, 29th.—Royal Institution, 3. "Life in Motion, or the Animal Machine," by Professor John G. McKendrick.

THURSDAY, 31st.—Royal Institution, 3. "Life in Motion, or the Animal Machine," by Professor John G. McKendrick.

SATURDAY, JAN. 2nd.—Royal Institution, 3. "Life in Motion, or the Animal Machine," by Professor John G. McKendrick.

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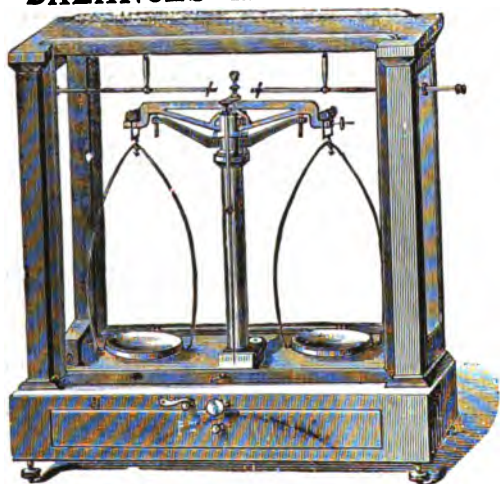


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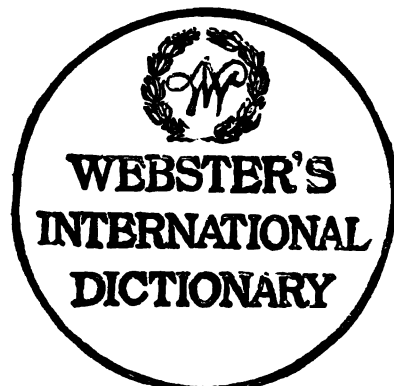
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